STUDIES IN ALKYLPALLADIUM CHEMISTRY, INCLUDING DEVELOPMENT OF THE NEW OXIDATION STATE, +IV

By

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This thesis contains no material which has been accepted for the award of any other degree or diploma in any University, and to the best of my knowledge, contains no copy or paraphrase of material previously presented by another person, except where due reference is made in the text.

Peter Byers.

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If you can look into the seeds of

time and say which grain will grow

and which will not, speak then to me.

William Shakespeare.

CONTENTS

ABSTRACT

This thesis describes the development of convenient and systematic routes to a wide range of monomethylpalladium(II) and dimethylpalladium(II) complexes of nitrogen donor ligands, and the first development of an extensive chemistry of alkylpalladium(IV) complexes. The work reported here has important implications for catalytic processes employing palladium, and for the future development of the new oxidation state, +IV, in organopalladium chemistry.

The synthesis and characterisation of $\{PdMe_2(L_n)\}$ and $\{PdMeX(L_n)\}$ complexes is described, with 2,2'-bipyridyl (bipy), 1,10-phenanthroline (phen), and alkane bridged bidentate ligands as L_2 and tridentate ligands as L_3, where L_2 and L_3 contain combinations of the N-donor heterocycles N-methylimidazol-2-yl, pyridin-2-yl and pyrazol-1-yl. Tridentate ligands were initially employed to assess the ability of palladium(II) to adopt coordination numbers greater than four. The reaction of $\{PdMe_2(L_n)\}$ with various organohalides (RX) has been studied, and has led to the detection, isolation and characterisation of the first hydrocarbylpalladium(IV) complexes.

The complexes $\{PdMe_2(L_n)\}$ and $\{PdMeI(L_n)\}$ have been synthesised using methyllithium. During development of these routes, the complexes $\{PdMe_2(\mu\text{-pyridazine})\}_n$ and $\{PdMe(\mu\text{-}X)(SMe_2)\}_2$ (X=Cl,Br,I) were also isolated, and reaction of these complexes with ligands (L_n) give dimethylpalladium(II) and methylpalladium(II) complexes, respectively. The iodo-bridged dimer $\{PdMe(\mu\text{-}I)(SMe_2)\}_2$ has also been used to prepare cationic complexes by reaction with $AgBF_4$ followed by addition of bipy, or by direct reaction with 2,2':6',2"-terpyridyl (terpy).

The halogeno-dimers $\{PdMe(\mu\text{-}x)(SMe_2)\}_2$, with square planar geometry for Pd(II), have been characterised by near and far infrared and ^1H NMR spectroscopy, molecular weight determinations, and an X-ray structure analysis for $\{PdMe(\mu\text{-}Cl)(SMe_2)\}_2$. The dimethylpalladium(II) complex $\{PdMe_2(\mu\text{-pyridazine})\}_n$ is unstable at ambient temperature, and was characterised only by ^1H NMR spectroscopy.

The neutral complexes, {$PdMeX(L_n)$} (X=Me, halide), and cationic complexes, $[PdMe(S)(bipy)]BF_4$ (S=SMe_2, CH_3CN, γ-pic) and [PdMe(terpy)]I, were characterised by microanalysis, ^1H NMR spectroscopy, and, for square planar $[PdMe(\gamma\text{-pic})(bipy)]BF_4$, an X-ray structure analysis. ^1H NMR spectra for the alkane bridged bidentate ligand complexes, {$PdMeX(L_2)$} (X=Me, halide), at ambient temperature were consistent with rapid boat to boat inversion of the chelate ring, while spectra for the tridentate ligand complexes {$PdMeX(L_3)$} (X=Me, halide) were consistent with rapid exchange between free and bound donor groups. Both processes could be resolved upon cooling, and low temperature solution state conformations determined. ^1H NMR spectra of the cationic complexes $[PdMe(S)(bipy)]BF_4$ also displayed variable temperature behaviour, consistent with site exchange of the Pd-S and Pd-Me groups.

Synthesis of the complexes {$PdMeI(L_2)$} was also accomplished by reaction of MeI with the corresponding dimethylpalladium(II) complex {$PdMe_2(L_2)$}, and led to the *in situ* detection of palladium(IV) intermediates, and to the subsequent isolation and characterisation of the first hydrocarbylpalladium(IV) complexes.

Reaction of MeI with {$PdMe_2(L_2)$} gave the isolable complexes {$Pd^{IV}Me_3I(L_2)$} for L_2=bipy and phen only, although neutral, and in some instances, cationic complexes, were spectroscopically detected for most of the other bidentate ligand complexes studied. The reaction of MeI with the tridentate ligand complexes {$PdMe_2(L_3)$}, on the other hand, produced the cations $[Pd^{IV}Me_3(L_3)]I$, which could be isolated for **all** tridentate ligands studied. The reaction of organohalides (RX) with {$PdMe_2$((pyridin-2-yl)bis(N-methylimidazol-2-yl)methane)} to give the stable cations $[Pd^{IV}Me_2R(pymim_2CH)]X$ was also studied, and the reaction of $PhCH_2Br$ with {$PdMe_2(bipy)$} produced the neutral complex {$Pd^{IV}Me_2(CH_2Ph)Br(bipy)$}.

The neutral complexes {$PdMe_2RX(L_2)$} were characterised by microanalysis, ^1H NMR spectroscopy, molecular weight determinations, and for {$PdMe_3I(bipy)$} by an X-ray structure determination. The kinetics of oxidative addition of MeI to {$PdMe_2(bipy)$} and reductive elimination of ethane from {$PdMe_3I(bipy)$} have been studied, and in both cases reaction proceeds *via* a polar intermediate, and an estimate

of the Pd(IV)-Me bond strength has been determined. The cationic complexes $[PdMe_2R(L_3)]X$ were characterised by microanalysis, ^1H NMR spectroscopy, and by an X-ray crystallographic study of the isostructural cations $[MMe_3(pz_3CH)]I$ (M=Pd, Pt). For both isolated and *in situ* detected neutral and cationic complexes a facial arrangement of the organogroups is proposed.

CHAPTER 1

INTRODUCTION

The chemistry of palladium is dominated by the 0(d^{10}) and +2(d^8) oxidation states, and although chemistry in the +1(d^9) and +4(d^6) states is established, examples are not numerous. Similarly, authenticated examples of palladium in the +3(d^7) and +5(d^5) oxidation states are extremely rare,[1] and in some instances, complexes which appear to possess the d^7 configuration for palladium have been shown to be mixed oxidation state (+2,+4) complexes.[1]

The divalent state is by far the most common for palladium,[1-4] and although Pd^{II} is generally regarded as a class b (soft) metal, reflected in its rich sulphur and phosphorus donor ligand chemistry, complexes with hard ligands are also known. Palladium(II) complexes are almost invariably diamagnetic and, with few exceptions, square planar geometry is adopted. Square planar geometry is also encountered for palladium(0) complexes, with chemistry in this oxidation state most widely represented by phosphine complexes.[5] The tetravalent oxidation state is rare,[1] and the few well characterised Pd(IV) complexes exhibit octahedral geometry. It is interesting to note that, in contrast to Pd(0) and Pd(II), phosphine donor ligands play a very minor role in Pd(IV) chemistry.

The most characteristic feature of palladium is the similarity of its chemistry to that of its 5d congener platinum, and includes atomic radii and bond lengths, *e.g.* M-Cl in $K_2[MCl_4]$ is 2.318 for M=Pd and 2.316Å for M=Pt.[2a] However two distinctive differences in their chemistries is the greater lability of palladium, and the pronounced instability of palladium in the tetravalent oxidation state. The greater lability for palladium is reflected in its increased reactivity compared with platinum, and is related to the ease with which it can increase its coordination number in solution. This particular feature has been invoked to explain exchange mechanisms[2a,6] and catalytic properties[3,7] of palladium complexes. Although palladium(IV) complexes are rare compared with the extensively developed palladium(II) and platinum(IV) chemistry,[8] this oxidation state is accessible, *albeit* unstable, and has been implicated in several stoichiometric and catalytic reactions.[2b,4,9]

The slow development of organotransition metal chemistry may be related to the early belief that transition-metal-carbon bonds were weak, a view supported by

calculations,[10] and led to the generalisation that organotransition-metal complexes are less stable than their main group analogues.[11] However, it is now recognised that transition-metal-carbon bonds are of comparable strength (160-350 $kJmole^{-1}$)[12] to main group metal-carbon bonds, and the observed instability is of kinetic origin. The availability of variable oxidation states and coordination numbers results in the operation of facile, low energy decomposition routes which are denied to main group analogues. These routes include 1,1-reductive elimination, β-hydrogen elimination and homolysis of the M-C bond, scheme 1.

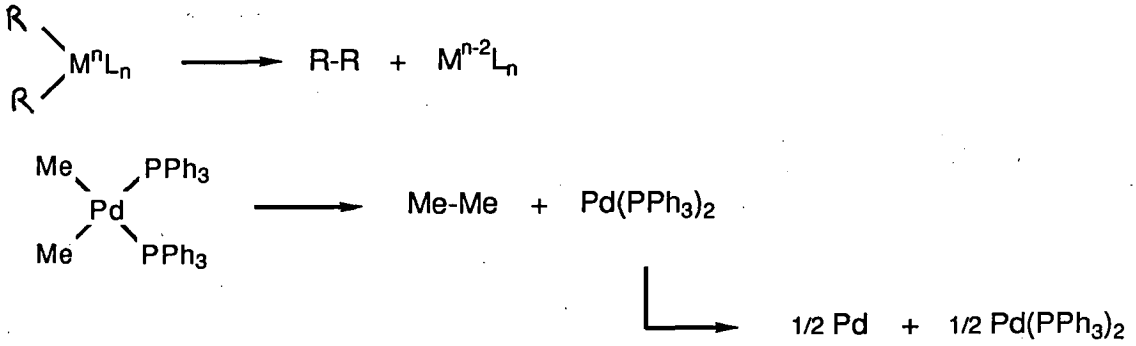
Organopalladium(II) complexes are far less numerous than organoplatinum(II) complexes due mainly to their lower stability and higher reactivity. Indeed, while organoplatinum chemistry involving Pt-C σ bonds commenced in 1907 with the report of $\{Pt^{IV}Me_3I\}_4$,[16] the first organopalladium complex was not prepared until half a century later,[17] and the first simple alkyl derivatives shortly after that.[18] It is not surprising, therefore, that most synthetic organopalladium work has dealt with complexes where this reactivity towards decomposition has been attenuated, *e.g.* β-hydrogen elimination can be avoided by the use of organic ligands which lack β-hydrogens, or may be restrained by formation of a metallacycle. The use of bulky ancillary ligands, particularly phosphines, also increases the inertness of the complexes.

Preparation of organopalladium(II) complexes can be readily accomplished by transmetallation, oxidative addition, or cyclometallation reactions, and by attack of nucleophiles on a coordinated olefin, scheme 2.

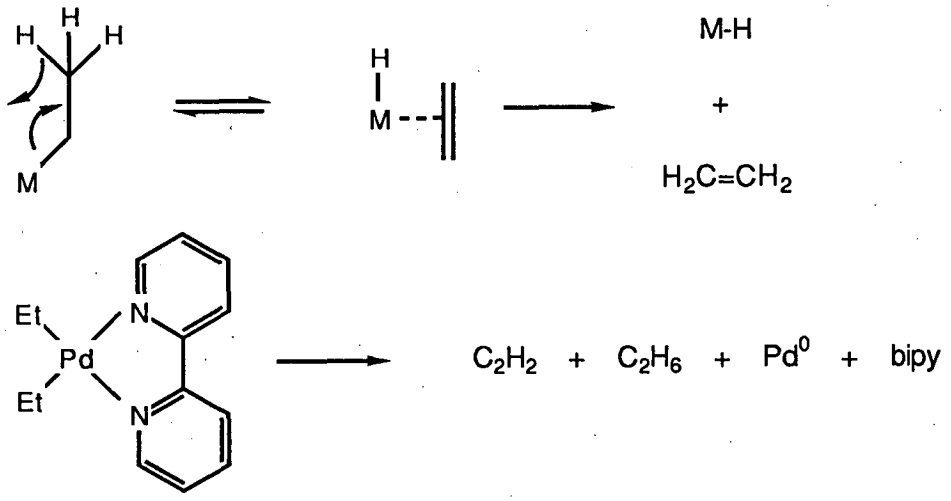
The formation of an organopalladium(II) complex, coupled with the propensity of the Pd-C σ bond to insert unsaturated molecules and the availability of several low energy decomposition routes, forms the basis of many useful organic syntheses.[22-24] For example, cyclometallation reactions frequently afford stable isolable complexes owing to the chelating nature of the ligand, and their synthetic usefulness is a result of subsequent reactions, such as insertion reactions, equation 1,[25] or coupling reactions, equation 2.[26] Ryabov has recently reviewed the application of cyclopalladated

Scheme 1

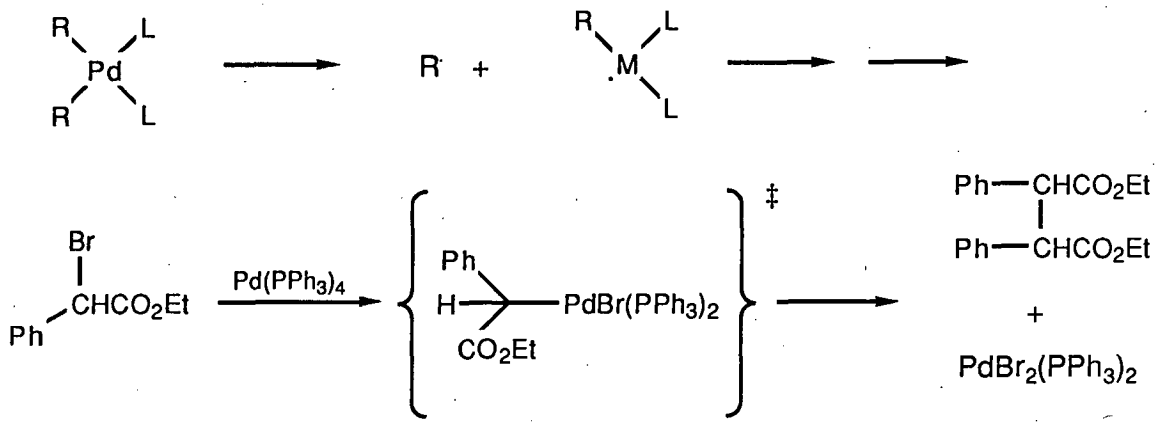
1,1-Reductive Elimination.[13]



β–Hydrogen Elimination.[14]



Homolysis.[15]



Scheme 2.

Transmetallation.[19]

$$2\ RM + \{PdX_2(L_2)\} \longrightarrow \{PdR_2(L_2)\} + 2\ MX$$

$$2\ MeLi + \{PdCl_2(PPh_3)_2\} \longrightarrow \textit{cis}\text{-}\{PdMe_2(PPh_3)_2\} + LiCl$$

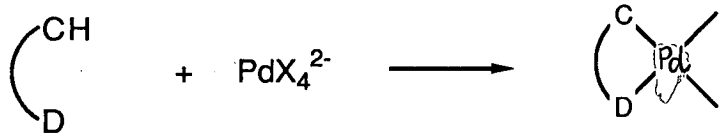
Oxidative Addition.[20]

$$R'X + PdL_n \longrightarrow \{PdR'X(L_2)\}$$

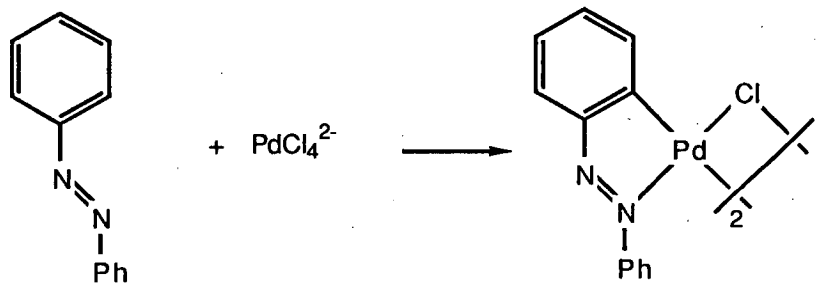
(n=2-4)

$$MeI + Pd(PPh_3)_4 \longrightarrow \textit{trans}\text{-}\{PdMeI(PPh_3)_2\}$$

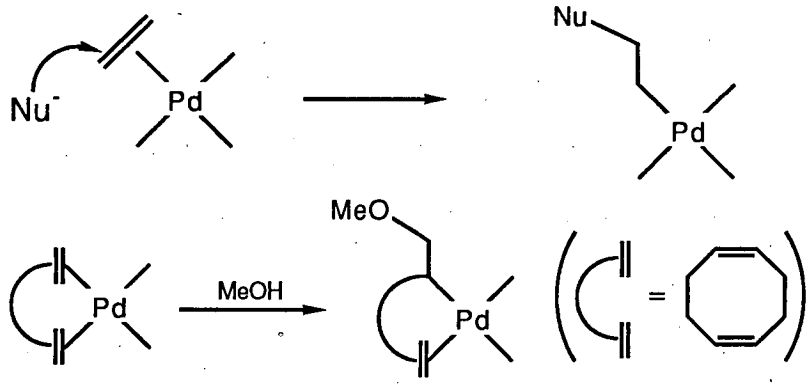
Cyclometallation.[21]



D=for example, P, N, S

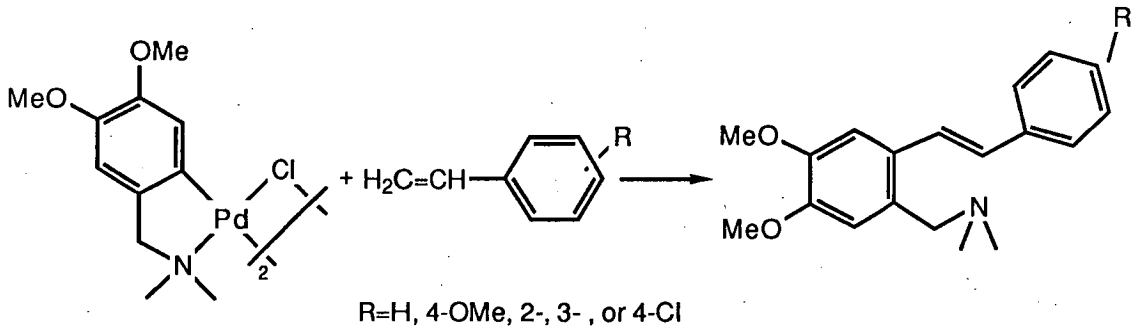


Nucleophilic Attack on a Coordinated Olefin.[17]



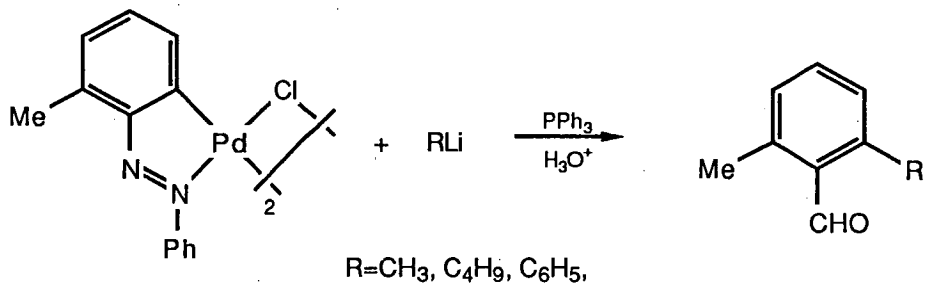
complexes in organic synthesis,[27] and of particular interest is the major role that N-donor ligands play in cyclopalladation in organic synthesis.[28]

Equation 1.



R=H, 4-OMe, 2-, 3- , or 4-Cl
2-, 3-, or 4-NO_2

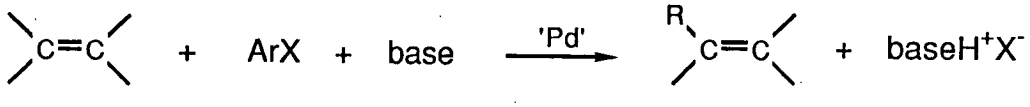
Equation 2.



R=CH_3, C_4H_9, C_6H_5,
$CH(CH_3)_2$, C_3H_7

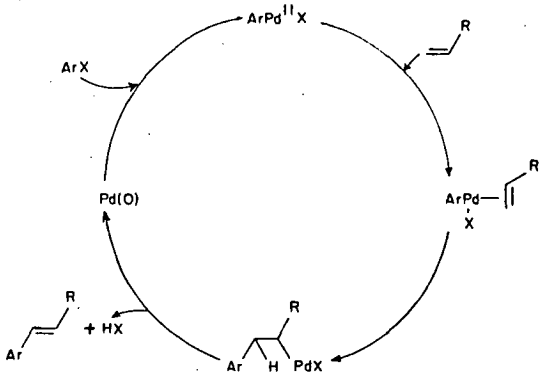
The characteristics of readily available oxidation state (0,II), flexible coordination number, kinetic lability, and affinity for a wide range of donor types, combine to make palladium an extremely effective and versatile catalyst.[29] Indeed, palladium is known to participate in a wide and diverse range of catalytic reactions,[9,23,24,30] *e.g.* olefin-arylation, equation 3,[31] and has been applied to the total synthesis of many complex organic molecules,[32] *e.g.* the synthesis of Prostaglandins.[32C]

Equation 3.



Catalysis by palladium is believed in many instances to involve the transient formation of a Pd-C σ bond which subsequently undergoes further reactions, *e.g.* insertion reactions, followed by liberation of the product(s). For example, olefin-arylation can be described by the catalytic cycle depicted in scheme 3,[31,32b] and involves formation of a Pd-C σ bond, *via* oxidative addition of RX, followed by insertion of an olefin and β-hydrogen elimination to yield the substituted olefin. Regeneration of the palladium catalyst in the final step is important, and differentiates **catalytic** reactions from **stoichiometric** reactions (*e.g.* equations 1 and 2). Reactions of the latter type are generally considered synthetically less useful than catalyses,[23] owing to the consumption of stoichiometric quantities of rather expensive palladium(II) complexes. Only a few palladium substrates are used frequently in catalytic reactions,[23] with $\{Pd(PPh_3)_4\}$ appearing to be the reagent of choice, although catalysis using palladium complexes containing the N-donor ligand bipy have been reported in some instances.[33]

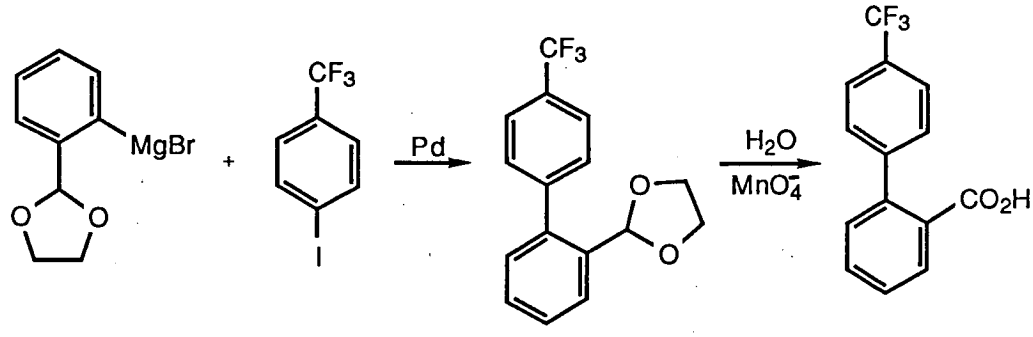
Scheme 3. Palladium Catalysed Arylation of Olefins (from ref 32b)



The formation of a carbon-carbon bond represents a critical operation in the synthesis of organic molecules, and the palladium mediated cross coupling of an organohalide with an organometal represents an extremely straightforward and efficient method for forming such bonds,[34] *e.g.* palladium catalysed cross coupling has been

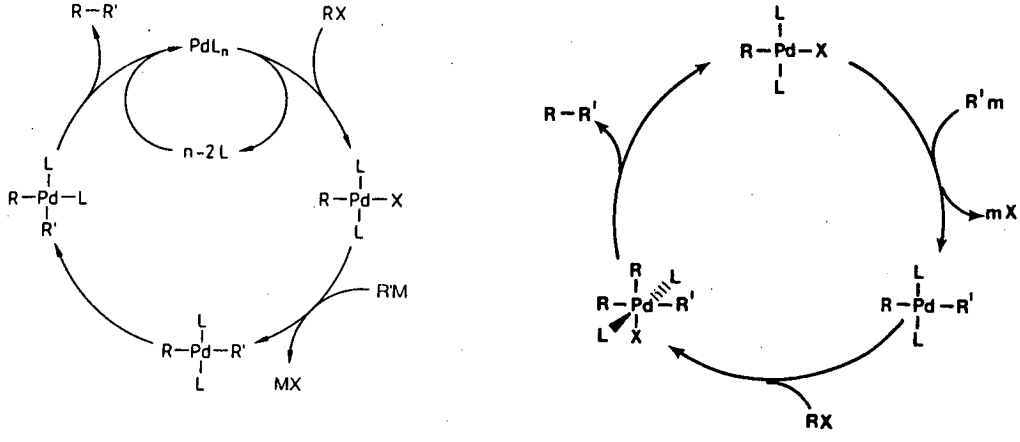
used for the preparation of trifluoromethyl substituted biphenylbicarboxylic acids, scheme 4, said to be useful in lowering blood serum cholesterol levels.[35]

Scheme 4.



It has been proposed that the cross coupling reaction involves a palladium(0)-palladium(II) cycle,[34] scheme 5a, although evidence has been obtained supporting a palladium(II)-palladium(IV) cycle for specific combinations of RX and RM,[36] scheme 5b. In either case, organopalladium(II) intermediates {$PdR_2(L_2)$} and {$PdRX(L_2)$} (R=organogroup, X=halide) appear to be involved.

Scheme 5. Palladium Catalysed Cross Coupling Reaction (from ref. 34, 36)



Despite the importance of N-donor ligands in cyclometallation reactions and, in some instances, catalytic reactions, and the extensively developed platinum(II) and platinum(IV) chemistry, remarkably few **simple** dialkyl- and monoalkylpalladium(II) complexes have been prepared. Indeed, at the commencement of this study nitrogen donor complexes were limited to $\{PdR_2(bipy)\}$ (R=Me,[19] CF_3,[37] Et,[14] CH_2CMe_3[38]), $\{Pd(CH_2CH_2CH_2CH_2)(L_2)\}$ (L_2=bipy, tmeda),[39] $\{PdMeX(bipy)\}$ [X=Cl (preparative procedure not given),[40] I (preparation doubtful)[37]] and $\{Pd(CH_2CMe_3)Br(bipy)\}$.[39] This is surprising as these complexes and their reactions may serve as models for the elucidation of palladium mediated reactions, in particular the cross coupling reaction.

Thus, the research reported in this thesis describes an investigation of the organometallic chemistry of palladium(II) with polydentate N-donor ligands, and the simplest of alkyl groups, methyl. Most of the ligands used are flexible, so that the usual square planar geometry is available to palladium, and contain the N-donor heterocyclic rings N-methylimidazole, pyridine or pyrazole. These donor rings were chosen because of their varying basicity, N-methylimidazole > pyridine > pyrazole, and varying ring sizes, *i.e.* five membered (N-methylimidazole, pyrazole) and six membered (pyridine). Further, the ligands can be grouped into two main categories, **bidentate ligands**, *e.g.* $py_2C{=}CH_2$ and py_2CH_2, and **tridentate ligands**, *e.g.* py_3CH. The former were chosen as they are analogous to bipy, but more flexible, while the latter allows a study of the tendency for Pd(II) to form higher coordination complexes,[41] at least in the solution state.

Preparation of the organometallic derivatives $\{PdMe_2(L_2)\}$ and $\{PdMeX(L_2)\}$ (X=halide, L_2=N-donor ligand) has been attempted using two methods, **transmetallation** and **oxidative addition** reactions. Transmetallation reactions with organometals such as MeLi and MeMgI represents the classical route to methylpalladium(II) complexes, although frequently attempts to prepare monoalkylated complexes from organolithium reagents is unsuccessful.[42] Thus, preparation of monomethylpalladium(II) complexes has been attempted *via* oxidative addition reactions.

The participation of organopalladium intermediates in organic synthesis and catalysis is discussed further in the chapters to follow.

REFERENCES

1. Barnard, C.F.J., and Russell, M.J.H.,
"Palladium" in "Comprehensive Coordination Chemistry", Wilkinson, G., Gillard, R.D., and McCleverty, J.A. (Eds.), Pergamon Press, Oxford, **5** (1987) 1099.

2.(a) Maitlis, P.M., Espinet, P., and Russell, M.J.H.,
"Palladium: Introduction and General Principles" in "Comprehensive Organometallic Chemistry", Wilinson, G., Stone, F.G.A., and Abel, E.W. (Eds.), Pergamon Press, Oxford, **6** (1982) 233.

(b) *Ibid*
"Compounds with Palladium-Carbon σ Bonds", **6** (1982) 279.

3. Livingstone, S.E.,
"The Chemistry of Ruthenium, Rhodium, Palladium, Osmium, Iridium and Platinum", Pergamon Press, Oxford, (1973) 1274.

4. Maitlis, P.M.,
"The Organic Chemistry of Palladium", Vol 1, Academic Press, London, 1971.

5. Maitlis, P.M., Espinet, P., and Russell, M.J.H.,
"Complexes of Palladium(0)" in "Comprehensive Organometallic Chemistry", Wilkinson, G., Stone, F.G.A., and Abel, E.W. (Eds.), Pergamon Press, Oxford, **6** (1982) 243.

6. Langford, C.H., and Gray, H.B.,
"Ligand Substitution Processes", W.A. Benjamin Inc., New York, 1965.

7. See, for example,
Holton, R.A.,
Tetrahedron Lett., (1977) 355.

8. Jain, V.K., Rao, G.S., and Jain, L.,
Adv. Organomet. Chem., **27** (1987) 113.

9. Maitlis, P.M.,
"The Organic Chemistry of Palladium", Vol. 2, Academic Press, London, 1971.

10. Jaffe, H.H., and Doak, G.O.,
J. Chem. Phys., **21** (1953) 196.

11. Cotton, F.A.,
Chem. Rev., **55** (1955) 551.

12. Cotton, F.A., and Wilkinson, G.,
"Advanced Inorganic Chemistry", John Wiley and Sons, Chichester, 1980.

13. Milstein, D., and Stille, J.K.,
J. Am. Chem. Soc., **101** (1979) 4981.

14. Sustmann, R., and Lau, J.,
Chem. Ber., **119** (1986) 2531.

15. Stille, J.K., and Lau, K.S.Y.,
J. Am. Chem. Soc., **98** (1976) 5841.

16. Pope, W.J., and Peachey, S.J.,
Proc. Chem. Soc., **23** (1907) 86.

17. Chatt, J., Vallarino, L.M., and Venanzi, L.M.,
J. Chem. Soc., (1957) 3413.

18. Calvin, G., and Coates, G.E.,
Chem. Indust., **78** (1958) 160.

19. Calvin, G., and Coates, G.E.,
J. Chem. Soc., (1960) 2008.

20. Gillie, A., and Stille, J.K.,
J. Am. Chem. Soc., **102** (1980) 4933.

21. Cope, A.C., and Siekman, R.W.,
J. Am. Chem. Soc., **87** (1965) 3272.

22. Tsuji, J.,
"Organic Synthesis", Springer-Verlag, Berlin, 1975.

23. Tsuji, J.,
"Organic Synthesis with Palladium Compounds", Springer-Verlag, Berlin, 1980.

24. Heck, R.F.,
"Palladium Reagents in Organic Syntheses", Academic Press, London, 1985.

25. Brisdon, B.J., Nair, P., and Dyke,. S.F.,
Tetrahedron, **37** (1981) 173.

26. Murahashi, S., Tamba, Y., Yamamura, M., and Yoshimura, N.,
J. Org. Chem., **43** (1978) 4099.

27. Ryabov, A.D.,
Synthesis, (1985) 233.

28. See, for example,
Dehand, J., and Pfeffer, M.,
Coord. Chem. Rev., **18** (1976), 327.
Bruce, M.I.,
Angew Chem. Int. Ed. Engl., **16** (1977) 73.
Omae, I.,
Chem. Rev., **79** (1979) 287.
Newkome, G.R., Puckett, W.E., Gupta, V.K., and Kiefer, G.E.,
Chem. Rev., **86** (1986) 451.

29. Collman, J.P.,
Acc. Chem. Res., **1** (1968) 136.
Colquhoun, H.M.,
Chem. Ind. (1987) 612.

30. Trost, B.M., and Verhoeven, T.R.,
"Organopalladium Compounds in Organic Synthesis and in Catalysis" in "Comprehensive Organometallic Chemistry", Wilkinson, G., Stone, F.G.A., and Abel, E.W. (Eds.), Pergamon Press, Oxford, **8** (1982) 799.

31. Heck, R.F.,
Organic Reactions, **27** (1982) 345.

32(a) Tsuji, J.,

"Application of Palladium Catalyzed or Promoted Reactions to Natural Product Syntheses" in "Syntheses of Natural Products", Topics in Current Chemistry, Springer-Verlag, Berlin, **91** (1980) 29.

(b) Hegedus, L.S., Weider, P.R., Mulhern, T.A., Asada, H., and D'Andrea, S., *Gazz. Chim. Ital.*, **116** (1986) 213.

(c) Larock, R.C., Narayanan, K., Carlson, R.K., and Ward, J.A., *J. Org. Chem.*, **52** (1987) 1364.

Larock, R.C., and Srinivasan, B., *Tetrahedron*, **43** (1987) 2013.

33. Card, R.J., Liesner, C.E., and Neckers, D.C., *J. Org. Chem.*, **44** (1979) 1095.

Sustmann, R., Lau, J., and Zipp, M., *Tetrahedron Lett.*, **27** (1986) 5207.

34. Negishi, E., *Acc. Chem. Res.*, **15** (1982) 340.

Beletskaya, I.P., *J. Organomet. Chem.*, **250** (1983) 551.

Sheffy, F.K., Godschalx, J.P., and Stille, J.K., *J. Am. Chem. Soc.*, **106** (1984) 4833.

Stille, J.K., *Angew. Chem. Int. Ed. Engl.*, **25** (1986) 508.

Negishi, E., Takahashi, T., Baba, S., Van Horn, D.E., and Okukado, N., *J. Am. Chem. Soc.*, **109** (1987) 2393.

35. Wellcome Foundation Ltd., Eur. Pat. Appl., 59983 (1982).

36. Milstein, D., and Stille, J.K., *J. Am. Chem. Soc.*, **101** (1979), 4992.

Gillie, A., and Stille, J.K., *Ibid.*, **102** (1980) 4933.

Loar, M.K., and Stille, J.K.,

Ibid., **103** (1981) 4174.

Moravskiy, A., and Stille, J.K.,

Ibid., **103** (1981), 4182.

37. Maitlis, P.M., and Stone, F.G.A.,

Chem. Ind. (1962) 1865.

38. Diversi, P., Fasce, D., and Santini, R.,

J. Organomet. Chem., **269** (1984) 285.

39. Diversi, P., Ingrosso, G., Lucherini, A., and Murtas, S.,

J. Chem. Soc. Dalton Trans., (1980) 1633.

40. Chaudhury, N., Kekre, M.G., and Puddephatt, R.J.,

J. Organomet. Chem., **73** (1974) C17.

41. See, for example,

Canty, A.J., Chaichit, N., Gatehouse, B.M., and George, E.E.,

Inorg. Chem., **20** (1981) 4293.

Canty, A.J., Minchin, N.J., Healy, P.C., and White, A.H.,

J. Chem. Soc. Dalton Trans., (1982) 1795.

42. For example,

Uson, R., Fornies, J., and Navarro, R.,

Syn. React. Inorg. Metal-Org. Chem., **7** (1977) 235.

CHAPTER 2

DIMETHYLPALLADIUM(II) COMPLEXES

2.1 INTRODUCTION

The reaction of an organometal (RM) with a palladium(II) substrate represents the most frequently employed route to diorganopalladium(II) complexes.

$$\text{'Pd'} + 2\,\text{RM} \rightarrow \text{'PdR}_2\text{'} \qquad 2.1\text{-}1$$

Historically the organometal used is either a Grignard (RMgX) or organolithium (RLi) reagent, and which reagent is more convenient for a particular synthesis is difficult to determine *a priori*. However, in general, organolithium reagents are more reactive, give higher degrees of alkylation, and are preferred for reactions at low to room temperature. Grignard reagents, on the other hand, give lower degrees of alkylation, and are thermally more stable and thus allow reactions to be carried out at reflux.

A further significant difference between organomagnesium and lithium reagents, at least in the case of platinum salts, is that organolithium reagents give irreversible alkylation, whereas organomagnesium reagents involve a series of equilibria,[1] equations 2.1-2, 3. These reactions may provide an explanation for the frequent observation that preparation of diorganopalladium(II) complexes from Grignard reagents is only accomplished by the use of a large excess of the reagent.[2-4]

$$\{PtI_2(PEt_3)_2\} + MeMgI \leftrightarrow \{PtMeI(PEt_3)_2\} + MgI_2 \qquad 2.1\text{-}2$$

$$\{PtMeI(PEt_3)_2\} + MeMgI \leftrightarrow \{PtMe_2(PEt_3)_2\} + MgI_2 \qquad 2.1\text{-}3$$

For transmetallation reactions involving organolithium or magnesium reagents, the palladium(II) substrate used is almost invariably a dihalopalladium(II) complex, *i.e.* $\{PdX_2(L_2)\}$. The halogeno group (X) is frequently a chloride or bromide, or more rarely an iodide, and the ligand (L), frequently a phosphine, remains unchanged

during the reaction, equation 2.1-4. This preparative procedure was used for the preparation of the first diorganopalladium(II) complexes, by Calvin and Coates in the late 1950's,[5] and subsequently a variety of complexes of the form $\{PdR_2(L_2)\}$ have been prepared by a similar route,[2-12] for example equations 2.1-5, 6.

$$\{PdX_2(L_2)\} + n\,RM \rightarrow \{PdR_2(L_2)\} + MX \qquad 2.1\text{-}4$$

X=halide, L=for example, PR_3, bipy

n~2.5 for M=Li

n~5-7 for M=MgX

$$\{PdX_2(PEt_3)_2\} + 2\,RLi \rightarrow \{PdR_2(PEt_3)_2\} \qquad 2.1\text{-}5$$

X=Br, R=Me[4]; X=Cl, R=CH_2SiMe_3[7]

$$\{PdCl_2(dppe)\} + 2\,RLi \rightarrow \{PdR_2(dppe)\} \qquad 2.1\text{-}6$$

R=C_6F_5[8c]

A modification of this reaction, which has not been fully exploited, involves the reaction of ligands (L') with a diorganopalladium(II) substrate containing weak donor ligands, equation 2.1-7. The diorganopalladium(II) substrates were either generated *in situ*,[2,12,13a] *e.g.* $\{PdMe_2(PhCN)_2\}$,[2] equation 2.1-8, or were isolated and subsequently reacted with ligands,[13b,c] *e.g.* $\{Pd(C_6F_5)_2(dioxane)\}$,[13b,c] equation 2.1-9.

$$\{PdR_2(L_2)\} + 2\,L' \rightarrow \{PdR_2(L'_2)\} + 2\,L \qquad 2.1\text{-}7$$

$$\{PdCl_2(PhCN)_2\} + 7MeMgBr \rightarrow \text{'}PdMe_2(PhCN)_2\text{'} \xrightarrow{\downarrow 2\,L'} \{PdMe_2(L'_2)\} \qquad 2.1\text{-}8$$

L'=PPh_3, $P(OPh)_3$, dppe

$$\{Pd(C_6F_5)_2(dioxane)\} + 2\,L' \rightarrow \{Pd(C_6F_5)_2(L'_2)\} \qquad 2.1\text{-}9$$

L'=PhCN, COD, NBD[13b]

L'=for example, *o*, or *p*-$MeOC_6H_4NH_2$, *o*, or *p*-$OHC_6H_4NH_2$[13c]

The use of palladium(II) acetate† in place of the palladium(II) dihalides described above, has been reported by Tooze *et al.*[15] Tooze found that $\{Pd(OAc)_2\}$ reacts with R_2Mg (R=Me, CH_2SiMe_3, CH_2Ph) or RMgCl (R=CH_2SiMe_3, CH_2CMe_2Ph), in the presence of L=PMe_3 or L_2=dmpe to afford the complexes $\{PdR_2(L_2)\}$, equation 2.1-10. The interaction of palladium(II) acetate with various organomercury reagents has been used by Heck to alkylate alkenes,[16] for example equation 2.1-11, but the intermediate 'alkylpalladium' complexes were not characterised.

$$\{Pd(OAc)_2\} + R_2Mg\,/\,RMgCl + L \rightarrow \{PdR_2(L_2)\} \qquad 2.1\text{-}10$$

L=PMe_3, L_2=dmpe; R=Me, CH_2SiMe_3, CH_2Ph, CH_2CMePh

$$\{\quad Pd(OAc)_2\} + Hg(PhCH_2)(OAc) + CH_2{=}CHCH_2OAc \qquad 2.1\text{-}11$$

$$\downarrow$$

$$PhCH_2CH{=}CHCH_2OAc$$

A variation of the preceding methods has been reported by Ito *et. al.*,[17] and involves alkylation of $\{Pd(acac)_2\}$ with $AlR_2(OEt)$ (R=Me, Et, Pr^n) in the presence of donor ligands, L=PEt_3, PPh_2Me, dppe, equation 2.1-12. It was claimed[17] that this procedure was more convenient than conventional routes due to the isolation of the desired products directly from the reaction mixture without prior hydrolysis. This

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† palladium(II) acetate, $\{Pd(OAc)_2\}_3$, is trimeric in solution,[14a] and in the solid state,[14b] and is commonly abreviated as $\{Pd(OAc)_2\}$.

enabled the isolation of organopalladium(II) complexes which were susceptible to water, or were stable only at low temperature. An analogous reaction with L=bipy and R=Et has been employed for the preparation of $\{PdEt_2(bipy)\}$.[18]

$$\{Pd(acac)_2\} + 2\,L + AlR_2(OEt) \rightarrow \{PdR_2(L_2)\} \qquad 2.1\text{-}12$$

R=Me, Et, Pr^n; L=PEt_3, PPh_2Me, 1/2 dppe[17]

R=Et; L_2=bipy[18]

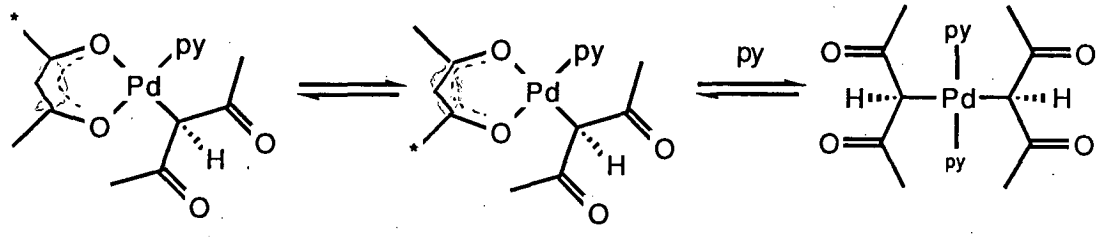
It is interesting to note, at this point, that while the use of organolithium reagents affords the *cis* (or occasionally *trans*) products $\{PdR_2(L_2)\}$ (L=unidentate tertiary phosphine), the use of organoaluminium reagents in the presence of L affords the corresponding *trans* isomers.[19,20]

$$\{PdCl_2(L_2)\} + RLi \rightarrow \textit{cis}\text{-}\{PdR_2(L_2)\}$$

$$\{Pd(acac)_2\} + AlR_2(OEt) + L \rightarrow \textit{trans}\text{-}\{PdR_2(L_2)\}$$

Palladium(II) complexes of β-dicarbonyls have also been used to prepare organopalladium(II) complexes with *C*-bonded acac$^-$ under extremely mild conditions, *e.g.* $\{Pd(acac)_2\}$ exhibited variable temperature ^1H NMR spectra in pyridine-D5 which were consistent with the equilibrium outlined below,[21] equation 2.1-13. Attempts to isolate the diorgano-intermediate from the equilibrium mixture failed.

Equation 2.1-13



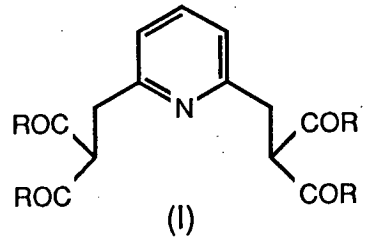
More successful was the reaction of N-donor ligands (L=py, 2-Mepy, $PhCH_2NH_2$, Bu^nNH_2, 1/2bipy) with $\{Pd(etac)_2 \cdot 1/2H_2O\}$ (etac=ethylacetoacetate†) to form the isolable complexes *cis*, *trans*-$\{Pd(etac\text{-}C^2)_2(L_2)\}$,[22] equation 2.1-14, although these complexes also readily liberated one donor molecule in $CDCl_3$ solution to give an equilibrium mixture similar to that of equation 2.1-13.

$$\{Pd(etac)_2 \cdot 1/2\ H_2O\} \ + \ 2\,L \ \rightarrow \ \{Pd(etac\text{-}C^2)_2(L_2)\} \qquad 2.1\text{-}14$$

L=py, 2-Mepy, $PhCH_2NH_2$, Bu^nNH_2, bipy

More recently Newkome and co-workers[23] have reported the preparation of the first stable palladium(II) complexes which contain two central-carbon-bonded acetylacetonato ligands. This was achieved by reaction of the chelating ligands displayed in figure 2.1-1 (I) with palladium(II) salts in the presence of a donor ligand, *e.g.* pyridine, equation 2.1-15. This reaction sequence has subsequently been used for the preparation of many similar complexes.[24,25]

Figure 2.1-1



(I)

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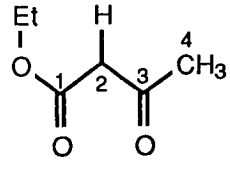
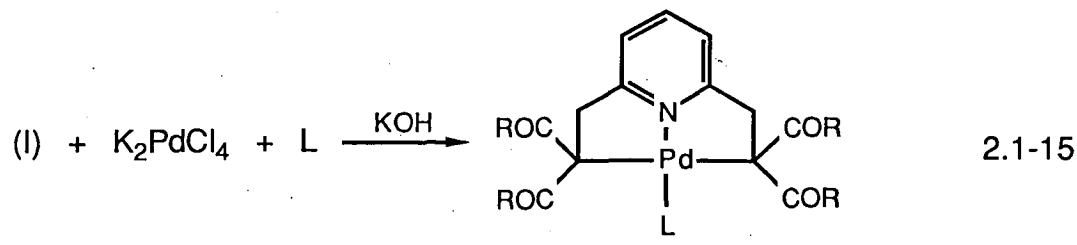
† etacH=ethylacetoacetate





2.1-15

While stable diorganopalladium(II) complexes are known, for example those in the preceding paragraph, or $\{PdMe_2(PEt_3)_2\}$ which may be sublimed in a vacuum at 40-50°C without decomposition,[4] the majority of reported examples exhibit moderate to low stability, especially at ambient temperature or in solution.

Calvin and Coates[4] in the first definitive paper on organopalladium(II) chemistry have noted and commented on the instability of $\{PdR_2(L_2)\}$ complexes. They reported that the most stable complexes are formed when the organic group is methyl, phenylethynyl, or phenyl groups bearing electron withdrawing substituents. Attempts to isolate organopalladium(II) derivatives with higher alkyl groups, *e.g.* ethyl or *n*-propyl, were not successful. Also, attempts to prepare *cis*-diarylpalladium(II) complexes failed, but preparation of the corresponding *trans* isomers was achieved, and several diaryl complexes bearing electron withdrawing groups on the aryl ring were prepared, for example:-

$$cis\text{-}\{PdCl_2(L_2)\} + RLi \not\rightarrow cis\text{-}\{PdR_2(L_2)\}$$

R=C_6H_5, L_2=chelating ligand *e.g.* bipy, dppe

$$\{PdCl_2(L_2)\} + RLi \rightarrow trans\text{-}\{PdR_2(L_2)\}$$

L=PEt_3, R=C_6H_5, *p*-$CF_3(C_6H_4)$, *p*-$C_6H_4.NMe_3^+I^-$

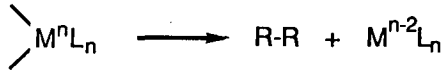
The effect that electron withdrawing substituents on the aryl ring have on the stability of $\{PdR_2(L_2)\}$ is striking. For example, while strong donor ligands, *e.g.* phosphines or bipy, are required to stabilize methyl derivatives,[4] poor ligands such as

COD, NBD or dioxane stabilize perhaloaryl derivatives,[13] and the homoleptic complex $[NBu^n]_2[Pd(C_6F_5)_4]$ has also been isolated.[26]

Ito *et. al.*[17] in a more recent study, prepared and investigated the thermolysis of the complexes $\{PdR_2(L_2)\}$ (R=Me, Et, Pr^n; L=PEt_3, PPh_2Me, 1/2dppe). They found that thermal stability of the complexes increased in the order Pr^n < Et < Me for the complexes with the same ligand, and PEt_3 < PPh_2Me < dppe for complexes with the same alkyl group. The reaction involving β-hydrogen abstraction was suggested as the operative mechanism in the decomposition of the higher alkyl complexes, while decomposition of the methyl derivatives was a result of 1,1-reductive elimination (to yield the coupled product CH_3CH_3) and α-elimination (to yield (CH_4 and C_2H_4)).

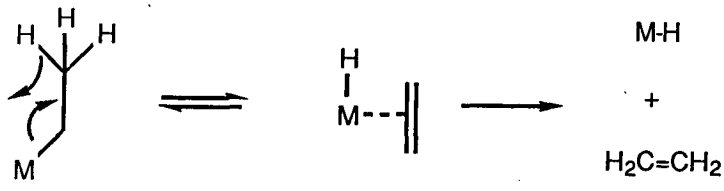
Elimination of R groups *via* 1,1-reductive elimination, equation 2.1-16, or β-hydrogen abstraction, equation 2.1-17, is extremely common for palladium,[27] and the reactions represent facile, low energy routes for the decomposition of $\{PdR_2(L_2)\}$ complexes.

<u>1,1-Reductive Elimination.</u>



2.1-16

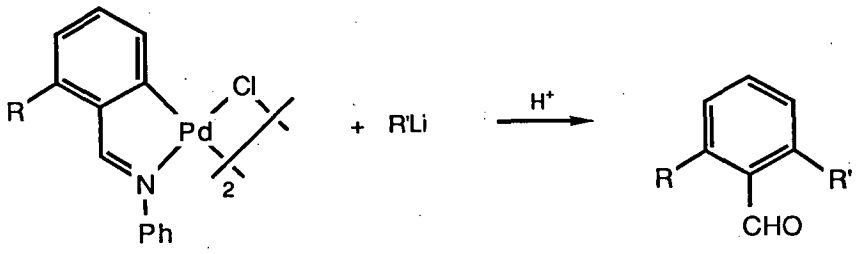
<u>β–Hydrogen Elimination.</u>



2.1-17

The availability of these low energy routes has been exploited in organic synthesis, as the formation of a C-C bond represents one of the most fundamental reactions in organic chemistry. For example, equation 2.1-18 depicts the preparation

of *o*-alkyl substituted benzaldehydes, which are otherwise difficult to prepare, in 60-65% yield by 1,1-reductive elimination of R groups.[28]



2.1-18

R=H, R'=Me; R=Me, R'=Me, Bu^n, Ph;
R=OMe, R'=Me

The preparation of stable organopalladium(II) complexes depends upon attenuating or blocking these decomposition routes. This can be achieved by avoiding R groups which contain β-hydrogens, for example CH_3 or CH_2CMe_3, equations 2.1-19, 20, or by forming complexes which have the *trans* configuration, equations 2.1-15, 21 (organo groups must be *cis* to each other to undergo 1,1-reductive elimination).[27] A detailed discussion of reductive elimination reactions can be found in chapter 5.

$$\{PdCl_2(L_2)\} + 2\,(Me_3XCH_2Li) \rightarrow \{Pd(CH_2XMe_3)_2(L_2)\} \qquad 2.1\text{-}19$$

L=PEt_3, X=Si[7]

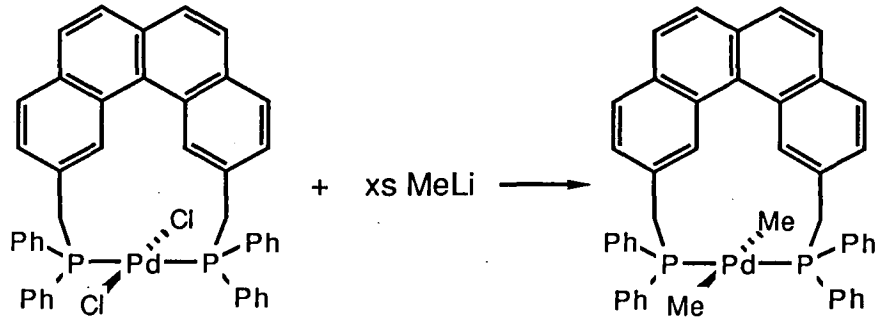
L=1/2 dppe, 1/2 bipy, PMe_2Ph, X=C[3]

$$\{PdCl_2(L_2)\} + 2\,MeLi \rightarrow \{PdMe_2(L_2)\} \qquad 2.1\text{-}20$$

L=for example, PEt_3, bipy, COD[4]

The preparation of stable organopalladium(II) complexes is also critically dependent upon the choice of ancillary ligands (L). It has been predicted[1a,30] that stable alkyl and acyl complexes are obtained when ligands which produce a large

crystal field splitting are used, for example phosphine and arsine based ligands, or bipy. This hypothesis is supported by the observation that nearly all stable diorganopalladium(II) complexes which contain simple alkyl or acyl organo-groups also contain phosphine or arsine based ligands, or bipy, as ancillary ligands.

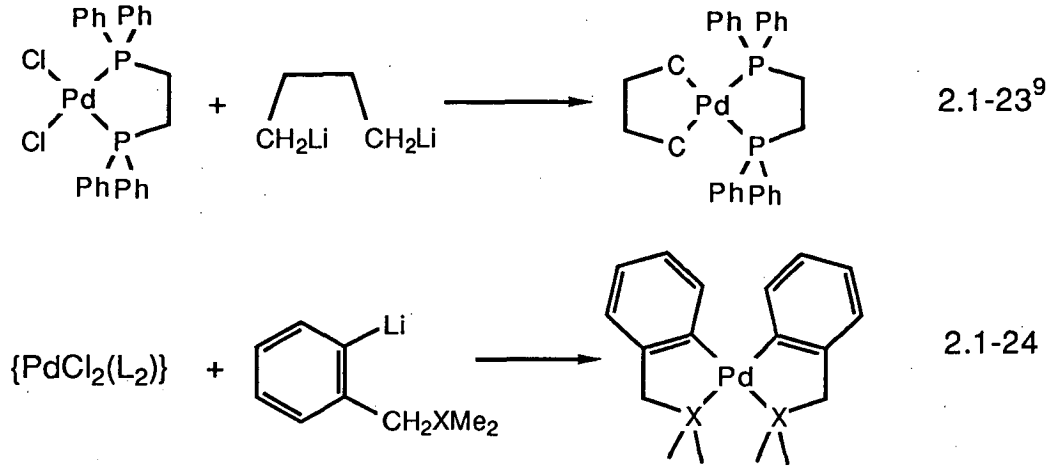


2.1-21[29]

Complexes containing R groups which lack β-hydrogens, *e.g.* methyl, may be further stabilised by the use of chelating ligands, *e.g.* dppe or bipy. The use of chelating ligands raises the energy barrier to the 1,1-reductive elimination pathway, which requires prior dissociation of a ligand to produce a coordinatively unsaturated intermediate,[27,31] equation 2.1-22.

$$cis\text{-}\{PdR_2(L_2)\} \rightarrow \text{'}PdR_2(L)\text{'} \rightarrow R\text{-}R + PdL_2 \qquad 2.1\text{-}22$$

Indeed, in general the formation of a chelate ring stabilizes organopalladium(II) complexes. This is exemplified by the reaction sequences depicted in equations 2.1-23, 24, where complexes containing β-hydrogens have been prepared. The ring compounds depicted in equations 2.1-23, 24 are usually more stable than the corresponding dialkyl complexes, *e.g.* $\{\overline{Pd(CH_2CH_2CH_2CH_2)}(dppe)\}$ as compared to $\{PdEt_2(dppe)\}$, because β-hydrogen abstraction is sterically inhibited by the more rigid ring alkyls.[32]



L=PhCN, X=N[10]
L=SEt_2, X=As[11]

Despite the recognition that the relative stability of diorganopalladium(II) complexes is of kinetic, rather than thermodynamic origin, remarkably few diorganopalladium(II) complexes containing N-based chelating ligands have been reported. Examples are limited to $\{PdR_2(bipy)\}$ (R=Me,[4] CF_3,[33] Et,[18] CH_2CMe_3[3]), $\{Pd(CH_2CHRCHRCH_2)(L_2)\}$ (R=H, L_2=bipy, tmeda†[9a]; R=Me, L_2=bipy, tmen[9b]), $\{Pd(biph)^{\#}(bipy)\}$,[12] and $\{PdMe_2(tmeda)\}$.[9c] This is surprising considering the extensively developed N-donor chemistry of alkylplatinum(II) complexes, and the potential to develop the chemistry of palladium in higher oxidation states, *viz.* Pd(IV). Consequently, one of the objectives of this study was to develop routes to dimethylpalladium(II) complexes with N-donor, chelating ancillary ligands, and to investigate their chemistry.

---

† tmeda=tetramethylethylenediamine

biph=two-fold deprotonated chelating biphenyl

2.2 PREPARATION AND CHARACTERISATION OF THE COMPLEXES $\{PdMe_2(L_2)\}$

2.2.1 Development of the Synthetic Routes.

From the preceding discussion it is clear that the main preparative route to dialkylpalladium(II) complexes involves reaction of a transmetallating reagent with a palladium(II) substrate, equations 2.2.1-1-3.

$$\{PdX_2(L_2)\} + n\,RM \rightarrow \{PdR_2(L_2)\} \qquad 2.2.1\text{-}1$$

M=Li, n=2-3; M=MgX, n=5-7

$$\{PdR_2(L_2)\} + 2\,L' \rightarrow \{PdR_2(L'_2)\} \qquad 2.2.1\text{-}2$$

$$\{Pd(acac_2)\} + AlR_2(OEt) + 2\,L \rightarrow \{PdR_2(L_2)\} \qquad 2.2.1\text{-}3$$

Potentially, the preparation of dimethylpalladium(II) complexes containing N-donor ligands can be achieved using MeLi, MeMgX, or $AlMe_2(OEt)$ as the transmetallating reagent. The choice of which reagent, and hence which route, to use is not immediately obvious, but becomes clear upon examination of the synthetic methods to these reagents. Thus, while the preparation of MeLi and MeMgI is achieved by direct reaction of MeI with Li or Mg metal,[34] equation 2.2.1-4, the preparation of $AlMe_2(OEt)$ involves a series of reactions,[34] one of which uses the toxic complex Me_2Hg, equations 2.2.1-5,6.

$$MeI + Li \rightarrow MeLi + LiI \qquad 2.2.1\text{-}4$$

$$MeI + Mg \rightarrow MeMgI$$

$$3Me_2Hg + 2\,Al \rightarrow 2AlMe_3 + Hg \qquad 2.2.1\text{-}5$$

$$Me_3Al + ROH \rightarrow AlMe_2(OR) + CH_4 \qquad 2.2.1\text{-}6$$

Further support for the preference of organolithium or magnesium reagents over aluminium reagents may be found in the observation that all† reported complexes $\{PdR_2(L_2)\}$ (R=alkyl group, L_2=chelating N-donor ligand), may be synthesised using Li or Mg reagents. It is also interesting to note that in the majority of cases, including cases where phosphine ligands are used, organolithium reagents are preferred over the corresponding magnesium reagent. Hence, in this study, preparation of dimethylpalladium(II) complexes containing chelating N-donor ligands was initially investigated using MeLi as the alkylating reagent, and the corresponding dihalopalladium(II) complexes as the palladium substrate.

Numerous attempts to prepare the complex $\{PdMe_2(pz_2CH_2)\}$ according to equation 2.2.1-7 (X=Cl) failed. This was due largely to the extremely low solubility of the palladium(II) substrate, $\{PdCl_2(pz_2CH_2)\}$, at the low reaction temperatures required (-50°C) to ensure stability of the organopalladium(II) product formed. Indeed, reactions performed at higher temperatures (-10→ 0°C) gave massive reduction, with isolation of palladium(0) only.

$$\{PdX_2(pz_2CH_2)\} + MeLi\,/\,LiI \not\rightarrow \{PdMe_2(pz_2CH_2)\}$$
$$(X=Cl, Br) \qquad \downarrow \qquad 2.2.1\text{-}7$$
$$\{PdI_2(pz_2CH_2)\} + Pd(0)$$

† one notable exception to this is the preparation of $\{Pd(C_3F_7)_2(bipy)\}$ which was prepared by the reaction of $(C_3F_7)I$ with $\{PdMe_2(bipy)\}$.[34]

In an attempt to increase the solubility of the palladium substrate, the complex $\{PdBr_2(pz_2CH_2)\}$ was prepared. However, the reaction of $\{PdBr_2(pz_2CH_2)\}$ with MeLi also failed to give an organopalladium(II) product. The products from these reactions were generally a mixture of $\{PdI_2(pz_2CH_2)\}$ (i.r. identification) and palladium metal. The complex $\{PdI_2(pz_2CH_2)\}$ presumably is formed by metathetical displacement of Cl^- or Br^- (in $\{PdX_2(pz_2CH_2)\}$) with I^-, present in solution as a byproduct from the formation of MeLi, from MeI and Li.

Clearly, the preparation of dimethylpalladium(II) complexes *via* a classical approach is not viable in this instance, due to the insolubility of $\{PdX_2(L_2)\}$ at low temperature, and the instability of $\{PdMe_2(L_2)\}$ at higher temperatures. Any successful preparation, therefore, will be dependent upon overcoming these two conflicting experimental conditions.

A method involving an *in situ* reaction between phosphine based ligands and a transient "$PdMe_2$" intermediate containing weak donor ligands has been reported by Garty and Michman[2] for the preparation of $\{PdMe_2(L'_2)\}$ complexes, equation 2.2.1-8. A similar procedure but with the addition of N-donor ligands may conceivably give analogous complexes, *e.g.* L'=pz_2CH_2 in equation 2.2.1-8.

$$\{PdCl_2(PhCN)_2\} + 7MeMgCl \rightarrow \text{'}\{PdMe_2(PhCN)_2\}\text{'} \xrightarrow{\downarrow 2L'} \{PdMe_2(L'_2)\} \quad (L'=PPh_3,\ P(OPh)_3,\ dppe) \qquad 2.2.1\text{-}8$$

In principle, the formation of a "$PdMe_2$" intermediate may be extended to include other dihalopalladium(II) substrates which contain weak donor ligands, for example, $\{PdCl_2(SMe_2)_2\}$. Indeed, reaction of the platinum analogues results in the formation of the dimethyl-complexes, $\{PtMe_2(COD)\}$ and $\{PtMe_2(\mu\text{-}SR_2)\}_2$ (R=Me, Et). These complexes have been widely used in the preparation of dimethylplatinum(II) complexes by the addition of donor ligands.

Attempted preparation of the corresponding dimethylpalladium(II) complexes containing the weak ligands COD and SR_2 (R=Me, Et) has been successful for COD only.[4] More recently, the reaction of $\{PdCl_2(SEt_2)_2\}$ with either MeLi or Me_2Mg in THF at -40°C has been reported. Steele and Vrieze[35] found that reaction of a suspension of $\{PdCl_2(SEt_2)\}$ with either MeLi or Me_2Mg gave a colourless solution, containing a white solid. Hydrolysis of this solution at -30°C, however, resulted in extensive decomposition with the formation of palladium metal.

While the nature of the intermediate species was not determined, it may be a '$PdMe_2$' complex, *e.g.* $\{PdMe_2(SEt_2)_2\}$, which, unlike its platinum analogue, is not stabilised sufficiently by the weak donor ligand SEt_2 to allow isolation, equation 2.2.1-9. Hence, addition of donor ligands (L'_2) immediately prior to hydrolysis may allow isolation of the more stable complexes $\{PdMe_2(L'_2)\}$, equation 2.2.1-10.

$$\{PdCl_2(SEt_2)_2\} + MeLi / Me_2Mg \xrightarrow{-40^\circ C} '\{PdMe_2(SEt_2)_2\}' \quad (2.2.1\text{-}9)$$

$$'\{PdMe_2(SEt_2)_2\}' \xrightarrow[2L']{-30^\circ C} \xrightarrow{H_2O} \{PdMe_2(L'_2)\} \quad (2.2.1\text{-}10)$$

L'_2=for example, bipy, dppe, or pz_2CH_2

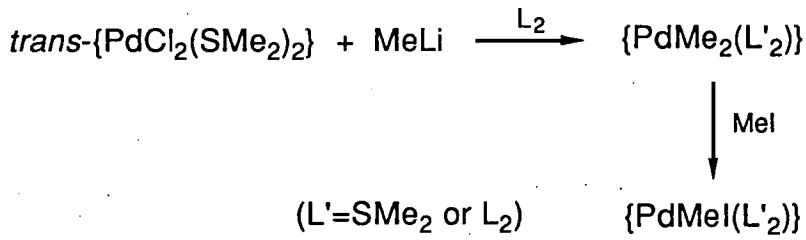
Modification of the procedure outlined above, involving reaction of *trans*-$\{PdCl_2(SMe_2)_2\}$† with MeLi, prepared from MeI and Li metal, followed by addition of pz_2CH_2, and hydrolysis gave the methylpalladium(II) product, $\{PdMeI(pz_2CH_2)\}$,

---

† to permit easier removal during work-up of the thioether generated during the reaction sequence, SMe_2 (b.pt. 38°C) was used in place of SEt_2 (b.pt. 92°C).

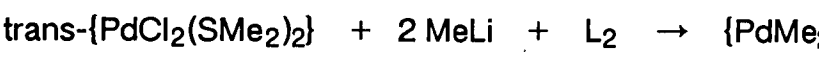
equation 2.2.1-11. The formation of a monomethyl-product is assumed to result from oxidative addition of MeI, present in solution from the preparation of MeLi, to a dimethylpalladium(II) species formed from reaction of MeLi with the dihalopalladium(II) substrate, equation 2.2.1-12. A more detailed discussion of the latter reaction, *i.e.* equation 2.2.1-12, may be found in chapter 3.

2.2.1-11

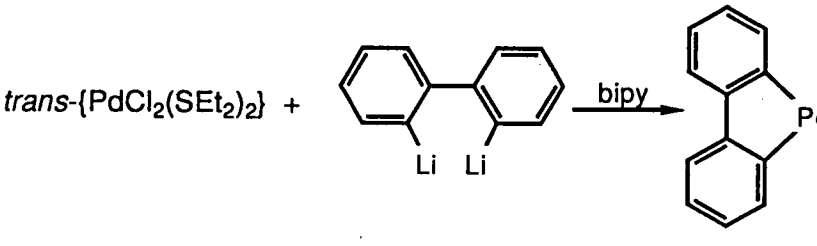


2.2.1-12

Preparation of a "methyl halide-free" MeLi solution, prepared from MeCl and a Li (1% Na) dispersion, and reaction with *trans*-{$PdCl_2(SMe_2)_2$} and pz_2CH_2 as above, gave the desired dimethylpalladium(II) complex, equation 2.2.1-13. Subsequently, this synthetic route was used to prepare numerous dimethylpalladium(II) complexes with a variety of ligands, and following the publication of this method,[36] Cornioley-Deuschel and von Zelewsky[12] have reported the preparation of {Pd(biph)(bipy)} by an analogous route, equation 2.2.1-14.



2.2.1-13



2.2.1-14

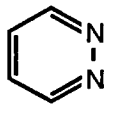
The method developed does, however, have two main limitations. Firstly, the reaction sequence works well only for ligands which exhibit significant solubility in diethyl ether at low temperature, essentially pyrazole and some pyridine based ligands of those studied. Addition of a THF solution of the ligand was not satisfactory, due to the difficulty encountered in isolating the unstable dimethylpalladium(II) products from the resultant diethyl ether/THF solvent mixture. Secondly, ligands which are sensitive to alkyllithium reagents, for example ketones or alcohols, are clearly not suitable.

An isolable dimethylpalladium(II) substrate, similar to that available for platinum, *e.g.* $\{PtMe_2(\mu\text{-}SMe_2)\}_2$, was sought to avoid these difficulties. The complex should contain a ligand that allows isolation of the dimethylpalladium(II) complex in high yield, and yet be readily displaced by a range of ligands; a suitable candidate was pyridazine†. Pyridazine has a bascity lower than that of pyrazole,[37] and hence lower than pyridine and N-methylimidazole#, and is known to form complexes with palladium[38] and other metals.[39] Also, importantly, pyridazine is easily prepared in high yield,[40] or may be obtained commercially.

Reaction according to equation 2.2.1-15 gives yellow-orange $\{PdMe_2(\mu\text{-}pyd)\}_n$ in 70-80% yield. Addition of donor ligands (L_2), dissolved in acetone or benzene, to this complex affords the corresponding complexes $\{PdMe_2(L_2)\}$ (L_2=chelating N-donor ligand), equation 2.2.1-16, in moderate to high yield. The reaction of $\{PdMe_2(\mu\text{-}pyd)\}_n$ with ligands (L_2) occurs under extremely mild conditions, and importantly, the complexes can be isolated without prior hydrolysis of

---

† pyridazine=



pK_a(pyridazine)=2.33, pK_a(pyrazole)=2.5, pK_a(pyridine)=5.6, pK_a(N-methylimidazole)=7.4.[39]

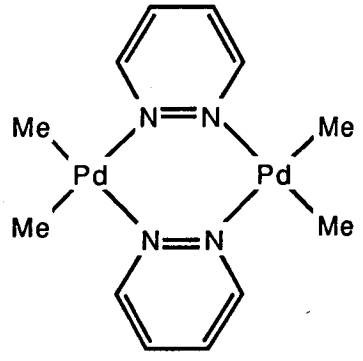
the solution. The pyridazine complex was also invaluable in the preparation of complexes which contain ligands sensitive to methyllithium, *e.g.* pymimCO.

$$trans\text{-}\{PdCl_2(SMe_2)_2\} + 2\,MeLi \xrightarrow[H_2O]{pyd} \{PdMe_2(\mu\text{-}pyd)\}_n \quad (70\text{-}80\ \%) \qquad 2.2.1\text{-}15$$

$$\{PdMe_2(\mu\text{-}pyd)\}_n + 2\,L_2 \xrightarrow[(benzene)]{acetone} \{PdMe_2(L_2)\} + 2\,pyd \qquad 2.2.1\text{-}16$$

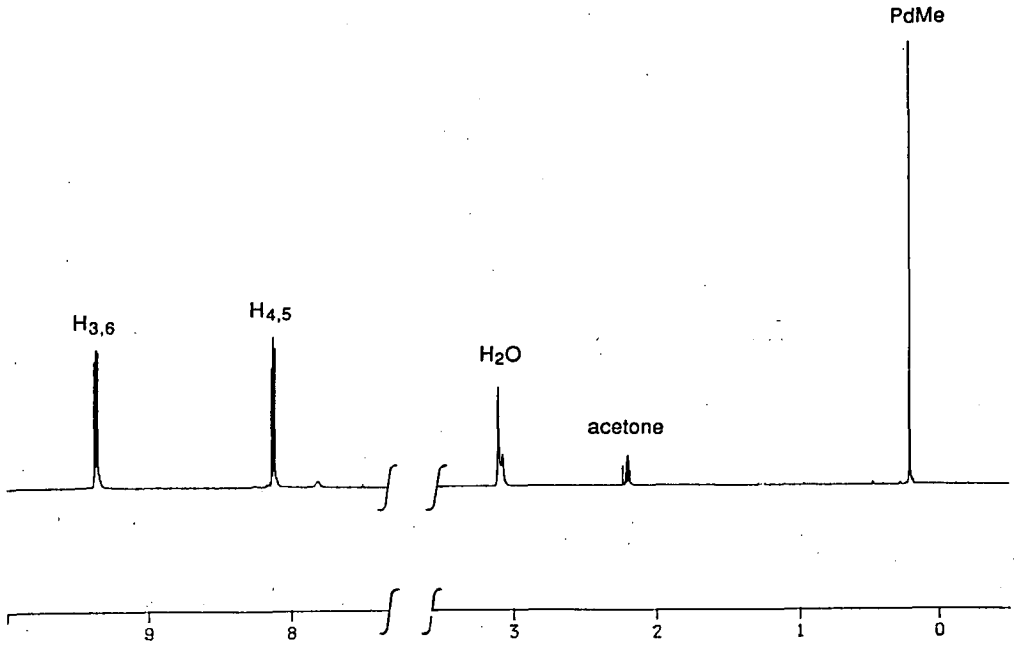
The complex $\{PdMe_2(\mu\text{-}pyd)\}_n$ readily decomposed in solution and as a solid upon standing at ambient temperature. Consequently, a correct microanalysis could not be obtained, although a rapidly recorded ^1H N.M.R. spectrum of the complex in acetone-D6 displayed a single Pd-Me environment and a single pyridazine environment in 2:1 ratio, figure 2.2.1-1. Consistent with this is the structure proposed below, figure 2.2.1-2†, although in the absence of molecular weight determinations the possibility of higher aggregates cannot be discounted.

Figure 2.2.1-2.



† pyridazine acting as a bridging ligand has been determined crystallographically for the ruthenium complex, $[\{Rh(C_5Me_5)\}_2(\mu\text{-}pyd)][ClO_4]_2$.[40]

Figure 2.2.1-1. ^1H N.M.R.of $\{PdMe_2(\mu\text{-pyd})\}_n$



2.2.2 Characterisation of the Complexes

Using the synthetic methods outlined above, and summarised below (equations 2.2.2-1,2), numerous dimethylpalladium(II) complexes containing a range of chelating N-donor ligands have been prepared.

$$trans\text{-}\{PdCl_2(SMe_2)_2\} + 2\ MeLi \xrightarrow{L_2} \{PdMe_2(L_2)\} \qquad 2.2.2\text{-}1$$

$$\{PdMe_2(\mu\text{-pyd})\}_n + L_2 \longrightarrow \{PdMe_2(L_2)\} \qquad 2.2.2\text{-}2$$

A correct microanalysis has been obtained for all† of the complexes, and, together with ^{1}H N.M.R. spectra, are consistent with the formulation $\{PdMe_2(L_2)\}$, *e.g.* ^{1}H N.M.R. spectra display a 2:1 ratio of PdMe and L_2 resonances (see chapter 4 for a detailed discussion of N.M.R. assignments).

The complexes varied in colour depending on the ligand present, with the formation of white complexes common for methane bridged ligands, *e.g.* R_2CH_2, or R_3CH, while ligands containing an unsaturated bridgehead group, *e.g.* $R_2C{=}O$, or $R_2C{=}CH_2$ gave red-orange complexes. The formation of coloured complexes in the latter case is most likely due to extensive charge delocalisation within the ligand.

The complexes $\{PdMe_2(L_2)\}$ also exhibited variable stability at ambient temperature, and this is illustrated, for example, by comparison of $\{PdMe_2(pz_2CH_2)\}$, which decomposed in acetone-D6 within a few minutes, with $\{PdMe_2(pymim_2CH)\}$, which under similar conditions was stable towards decomposition for several hours. However, prolonged storage in all cases is best accomplished at -20°C. Further, the instability of these complexes made recrystallisation extremely difficult, and indeed, could only be accomplished in a few cases using an acetone/hexane mixture with cooling. Microanalytically pure complexes were generally obtained directly from the reaction mixture.

Complexes prepared by either of the methods described in the preceding pages, including yields obtained, are listed in Table 2.2.2-1.

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† one exception to this is $\{PdMe_2(pz_2CH_2)\}$ for which a correct microanalysis could not be obtained. However, reaction of $\{PdMe_2(pz_2CH_2)\}$ with dppe gave white $\{PdMe_2(dppe)\}$, which displayed an identical ^{1}H N.M.R. spectrum to that for $\{PdMe_2(dppe)\}$, prepared using literature methods.[4]

Table 2.2.2-1. Preparation of $\{PdMe_2(L_2)\}$ Complexes and Yields Obtained

Ligand	Method of Preparation, Yield	Ligand	Method of Preparation, Yield
pz_2CH_2	a, 56%	$pymimC{=}CH_2$	b, 52%
pz_2CHMe	a, 61%	pymimCO	b, 46%
pz_2CMe	a, 75%	$pypzCH_2$	b, 54%
pz_3CH	a, 72%	$pzmimCH_2$	b, 54%
pz_4C	a, 60%	phen	b, 74%
bipy	a, 82%	pymim	b, 69%
$MeSCH_2CH_2SMe$	a, 65%	$pymim_2CH$	b, 75%
py_2CH_2	b, 71%	$mimpy_2CH$	b, 68%
py_2CHMe	b, 65%	$pypz_2CH$	b, 62%
py_2CMe_2	b, 62%	$mimpz_2CH$	b, 63%
$py_2C{=}CH_2$	b, 52%	py_3CH	b, 25%
mim_2CH_2	b, 79%	mim_2CO	b, 78%
mim_2CHMe	b, 49%	$mim_2C{=}CH_2$	b, 69%
$pymimCH_2$	b, 69%	pymimCHMe	b, 59%

(a) $\{PdCl_2(SMe_2)_2\} + MeLi + L_n \rightarrow \{PdMe_2(L_n)\}$

(b) $\{PdMe_2(\mu\text{-pyd})\}_n + L_n \rightarrow \{PdMe_2(L_n)\}$

REFERENCES

1. (a) Chatt, J., and Shaw, B.L.,
J. Chem. Soc., (1959) 705.

(b) Glockling, F., McBride, T., and Pollock, R.J.I.,
Inorg. Chim. Acta, **8** (1974) 77.

2. Garty, N., and Michman, M.,
J. Organomet. Chem., **36** (1972) 391.

3. Diversi, P., Fasce, D., and Santini, R.,
J. Organomet. Chem., **269** (1984) 285.

4. Calvin, G., and Coates, G.E.,
J. Chem. Soc., (1960) 2008.

5. Calvin, G., and Coates, G.E.,
Chem. Indust., (1958) 160.

6. Basolo, F., Chatt, J., Gray, H.B., Pearson, R.G., and Shaw, B.L.,
J. Chem. Soc., (1961) 2207.

7. Wozniak, B., Ruddick, J.D., and Wilkinson, G.,
J. Chem. Soc. (A), (1971) 3116.

8. (a) Uson, R., Fornies, J., Navarro, R., Garcia, M.P., and Bergareche, B.,
Inorg. Chim. Acta, 25 (1977) 269.

(b) Rausch, M.D., and Tibbetts, F.E.,
J. Organomet. Chem., **21** (1970) 487.

(c) Uson, R., Fornies, J., Gimeno, J., Espinet, P., and Navarro, R.,
J. Organomet. Chem., **81** (1974) 115.

9. (a) Diversi, P., Ingrosso, G., Lucherini, A., and Murtas, S.,
J. Chem. Soc. Dalton Trans., (1980) 1633.

(b) Diversi, P., Ingrosso, G., Lucherini, A., Lumini, T.,
Marchetti, F., Adovasio, V., and Nardelli, M.,
J. Chem. Soc. Dalton Trans., (1988) 133.

(c) de Graaf, W., Boersma, J., Grove, D., Spek, A.L., van Koten, G.,
Recl. Trav. Chim. Pays-Bas, **107** (1988) 299.

10. Kasahara, A., and Izumi, T.,
Bull. Chem. Soc. Jpn., **42** (1969) 1765.

11. Abicht, H., and Issleib, K.,
J. Organomet. Chem., **289** (1985) 201.

12. Cornioley-Deuschel, C., and von Zelewsky, A.,
Inorg. Chem., **26** (1987) 3354.

13.(a) Garcia, G., and Lopez, G.,
Inorg. Chim. Acta, **52** (1981) 87.

(b) De Haro, G., Garcia, G., Sanchez, G., and Lopez, G.,
J. Chem. Res. (S), (1986) 119.

(c) Lopez, G., Garcia, G., DeHaro, C., Sanchez, G., and Vallejo, M.C.
J. Organomet. Chem., **263** (1984) 247.

14.(a) Stephenson, T.A., Morehouse, S.M., Powell, A.R., Heffer, J.P.,
and Wilkinson, G.,
J. Chem. Soc., (1965) 3632.

(b) Skapski, A.C., and Smart, M.L.,
J. Chem. Soc. Chem. Commun., (1970) 658.

15. Tooze, R., Chiu, K.W., and Wilkinson, G.,
Polyhedron, **3** (1984) 1025.

16. Heck, R.F.,
J. Organomet. Chem., **37** (1972) 389.

17. Ito, T., Tsuchiya, H., and Yamamoto, A.,
Bull. Chem. Soc. Jpn., **50** (1977) 1319.

18. Sustmann, R., and Lau, J.,
Chem. Ber., **119** (1986) 2531.

19. Nakazawa, H., Ozawa, F., and Yamamoto, A.,
Organomet., **2** (1983) 241.

20. Ozawa, F., Ito, T., Nakamura, Y., and Yamamoto, A.,
Bull. Chem. Soc. Jpn., **54** (1981) 1868.

21. Ito, T., Kiriyama, T., Nakamura, Y., and Yamamoto, A.,
Bull. Chem. Soc. Jpn., **49** (1976) 3257.

22. Okeya, S., and Kawaguchi, S.,
Inorg. Chem., **16** (1977) 1730.

23. Newkome, G.R., and Kawato, T.,
Inorg. Chim. Acta, **37** (1979) L481.

24. Newkome, G.R., Kawato, T., Kohli, D.K., Puckett, W.E.,
Olivier, B.D., Chiari, G., Fronczek, F.R., and Deutsch, W.A.,
J. Am. Chem. Soc., **103** (1981) 3423.

25. Newkome, G.R. Kohli, D.K., and Fronczek, F.R.,
J. Am. Chem. Soc., **104** (1982) 994.

26. Uson, R., Fornies, J., Espinet, P., Navarro, R., Martinez, F.,
and Tomas, M.,
J. Chem. Soc. Chem. Commun., (1977) 789.
Uson, R., Fornies, J., Martinez, F., and Tomas, M.,
J. Chem. Soc. Dalton Trans., (1980) 888.

27. Yamamoto, A., Yamamoto, T., Komiya, S., and Ozawa, F.,
Pure. Appl. Chem., **56** (1984) 1621.

28. Murahashi, S., Tanba, Y., Yamamura, M., and Moritani, I.
Tetrahedron, Lett., **43** (1974) 3749.

29. Gillie, A., and Stille, J.K.,
J. Am. Chem. Soc., **102** (1980) 4933.

30. See, for example,
Coates, G.E., Green, M.L.H., and Wade, K.,
"Organometallic Compounds" Vol. 2, pg. 220.
Butler and Tanner Ltd., London, 1968.

Maitlis, P.M.,
"The Organic Chemistry of Palladium", Vol. 1, pg 64.
Academic Press, London, 1971.

31. Tatsumi, K., Hoffmann, R., Yamamoto, A., and Stille, J.K.,
Bull. Chem. Soc. Jpn., 54 (1981) 1857.

32. Cotton, F.A., and Wilkinson, G.,
"Advanced Inorganic Chemistry", pg 1119-1140.
John Wiley & Sons, Chichester, 1980.

33. Maitlis, P.M., and Stone, F.G.A.,
Chem. Indust., (1962) 1865.

34. Hagihara, N., Kumada, M., and Okawara, R.,
"Handbook of Organometallic Compounds",
W. A. Benjamin Inc., Amsterdam, 1968.

35. Steele, B.R., and Vrieze, K.,
Trans. Met. Chem., 2 (1977) 140.

36. Byers, P.K., and Canty, A.J.
Inorg. Chim. Acta, 104 (1985) L13.

37. Acheson, R.M.
"An Introduction to the Chemistry of Heterocyclic Compounds",
J. Wiley & Sons, Chichester, 1977.

38. Porter, J.J., Murray, J.L., and Takvorian, K.B.,
J. Heterocyclic Chem., 10 (1973) 43.

39. See, for example,

(a) Dixon, K.R.,
Inorg. Chem., 10 (1977) 2618.

(b) Uson, R., Oro, L.A., Esteban, M., Carmona, D., Claramunt, R.M.,
and Elguero, J.,
Polyhedron, 3 (1984) 213.

(c) Oro, L.A., Carmona, D., Lahoz, F.J., Puebla, M.P., Esteban, M., Foces-Foces, C., and Cano, F.H., *J. Chem. Soc. Dalton Trans.*, (1986) 2113.

40. Mizzoni, R.H., and Spoerri, P.E., *J. Am. Chem. Soc.*, 73 (1951) 1873.

CHAPTER 3

NEUTRAL AND CATIONIC MONOMETHYLPALLADIUM(II) COMPLEXES

3.1 INTRODUCTION

A specific area of organopalladium(II) chemistry that has received a great deal of attention in recent years is the preparation and reactions of monoorganopalladium(II) species. This is illustrated, for example, by the work of Heck.[1] Heck's group alone has investigated and developed eight organic syntheses catalysed by palladium substrates, all of which have monoorganopalladium(II) species as key intermediates,[1] *e.g.* the formylation of organohalides,[2] equation 3.1-1.

$$RX + CO + H_2 \xrightarrow[R'_3N]{\text{'Pd'}} RCHO + HX \qquad 3.1\text{-}1$$

'Pd'={$PdX_2(PPh_3)_2$} (X=halide)

Preparative routes to monoorganopalladium(II) species can be grouped into six general procedures, all of which are discussed below. Due to the instability of organopalladium complexes these procedures do not always yield isolable complexes, with the importance of palladium in organic synthesis often resulting from the instability of intermediates providing useful products. However, examples confirming the nature of these intermediates have been isolated for each preparative route. The preparative procedures are described in the following sections.

3.1.1 Transmetallation reactions with organomagnesium, -tin, and -mercury reagents.

An important and frequently employed route to organopalladium(II) complexes is the reaction of organometals, **RM**, with palladium(II) salts {$PdX_2(L_2)$}, equation 3.1.1-1. The first step of this reaction is readily accomplished by the use of Grignard reagents, **RMgX**, or more rarely, organolithium reagents, **RLi**. The second reaction

can be accomplished by the use of a large excess of the Grignard reagent, although the use of an organolithium reagent is generally more successful (chapter 2).

$$\underline{R}M + \{PdX_2(L_2)\} \xrightarrow{1} \{Pd\underline{R}X(L_2)\} + MX$$
$$\left(\xrightarrow[2\,\underline{R}M]{1} \{Pd\underline{R}_2(L_2)\} + MX \right) \qquad 3.1.1\text{-}1$$

The palladium substrate used is generally a dichloro-, dibromo- or, more rarely, a diiodopalladium(II) complex, $\{PdX_2(L_2)\}$. The ancillary ligands (L) are, in the preparation of stable products, strong donor ligands such as phosphines,[3,4,5] arsines,[3] seleno- and telluroethers,[6] or chelating ligands (*e.g.* 2.2'-bipyridyl).[3] The organopalladium(II) products formed, $\{PdRX(L_2)\}$, generally have, except in the case of *cis*-chelating ligands, the *trans* configuration. Attempts to prepare organopalladium(II) complexes without strong donor ligands result in decomposition at room temperature, *e.g.* equation 3.1.1-2.[7]

$$PdCl_2 + 2\,EtMgBr \xrightarrow{Et_2O} \begin{matrix} C_2H_4 + C_2H_6 + \\ Pd^0 + 2\,MgClBr \end{matrix} \qquad 3.1.1\text{-}2$$

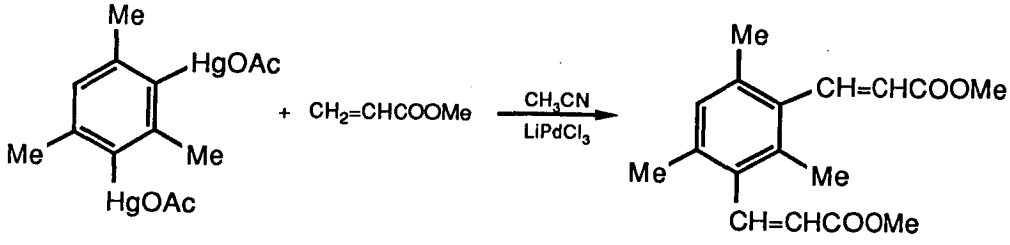
The use of Grignard reagents has several disadvantages. Firstly, they are air and moisture sensitive, and consequently are best used under anaerobic and anhydrous conditions; reactions are frequently performed under nitrogen in anhydrous diethyl ether. Secondly, they are expected to react with ligands containing groups sensitive to Grignard reagents, *e.g.* ketones, aldehydes, nitriles. Finally, it is not possible to prepare Grignard reagents which contain a range of organic functional groups *e.g.* esters, ketones, aldehydes.

Organomercurials and organotins also undergo facile transmetallation reactions, but, in contrast to Grignard reagents, they can tolerate many organic functional groups.

They are easily prepared using standard techniques, are thermally stable, and are insensitive to moisture and air.

While organomercurial[8] and organotin[9] reagents have been used to prepare and isolate monoorganopalladium(II) complexes, they are more frequently employed for the generation of *in situ* species. For example, Heck, in a series of papers,[10] utilized 'PdRX' (prepared from aryl mercury(II) reagents and palladium(II) salts), for the arylation of olefins, *e.g.* equation 3.1.1-3.

Equation 3.1.1-3



Further discussion of the preparation and reactions of transient monoorganopalladium(II) species does not fall within the overall scope of this report and may be found elsewhere.[11-13]

3.1.2 Oxidative addition of Organohalides, RX

An important and fundamental reaction in organometallic chemistry is **oxidative addition.** Oxidative addition is the term used to describe, regardless of mechanism, the oxidation of a metal, M, by addition of a molecule X-Y. Both one and two electron oxidative additions are recognised, equations 3.1.2-1 and 3.1.2-2 respectively, and an important feature of these reactions is that an increase in the oxidation state of the metal is usually accompanied by an increase in the coordination number.

$$M + X\text{-}Y \rightarrow X\text{-}M + Y\text{-}M \text{ or } X\text{-}M\text{-}M\text{-}Y \qquad 3.1.2\text{-}1$$

$$M + X\text{-}Y \rightarrow X\text{-}M\text{-}Y \text{ or } X\text{-}M^{+}Y^{-} \qquad 3.1.2\text{-}2$$

The reverse of the above reaction is termed **reductive elimination.** In this reaction the oxidation state and the coordination number of the metal decreases, *e.g.* as in equation 3.1.2-3.

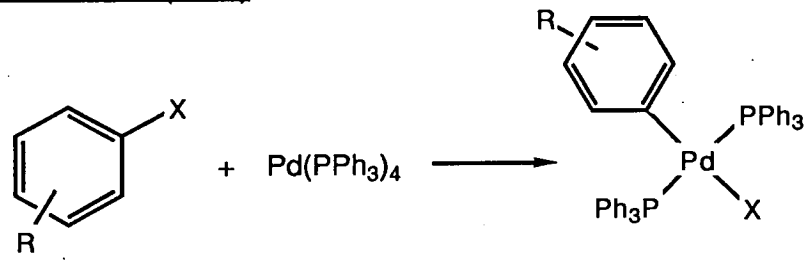
$$X\text{-}M\text{-}Z \rightarrow M + X\text{-}Z \qquad 3.1.2\text{-}3$$

The oxidative addition of various organohalides, *e.g.* aryl halides,[14] pyridyl halides,[15] benzyl halides,[16] and alkyl halides[17] to Pd(0) substrates has been utilised to prepare many examples of monoorganopalladium(II) complexes, equations 3.1.2-4-7. In the majority of cases the palladium(0) substrate contains phosphine based ligands,[18] frequently PPh_3.

In recent years the palladium(0) complex of dibenzylideneacetone (dba) has been utilised. Examples of oxidative addition to $Pd(dba)_2$,[19] $Pd_2(dba)_3{\cdot}S$ ($S=CHCl_3$, C_6H_6, $C_6H_5(CH_3)$),[20] and Pd(bipy)(dba)[21] have been reported, equations 3.1.2-8-10. Oxidative addition, unless restricted by *cis*-chelating ligands, generally gives the *trans* configuration.

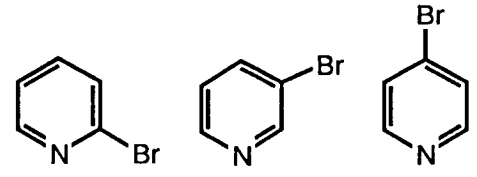
A second, less obvious route to monoorganopalladium(II) complexes is *via* reaction of an organohalide, RX, with a diorganopalladium(II) complex, $\{PdR_2(L_2)\}$. These reactions are believed to proceed *via* an oxidative addition-reductive elimination sequence, equation 3.1.2-11. Several examples of monoorganopalladium(II) complexes prepared by this route have been reported,[22] *e.g.* equation 3.1.2-12, but the Pd(IV) intermediate proposed has not been detected.

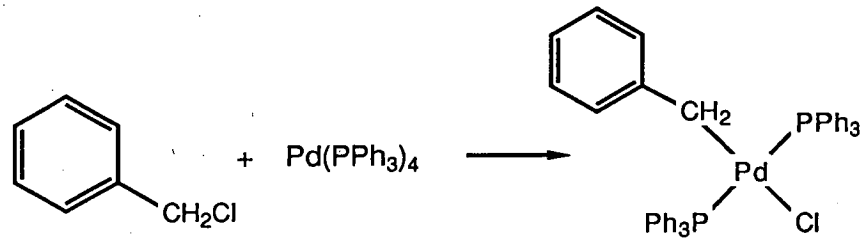
Equations 3.1.2-(4-10)



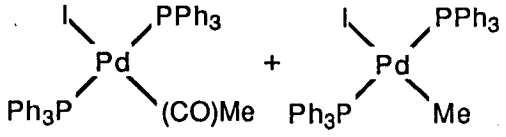
RBr + $Pd(PPh_3)_4$ ⟶ trans-{$PdRBr(PPh_3)_2$}

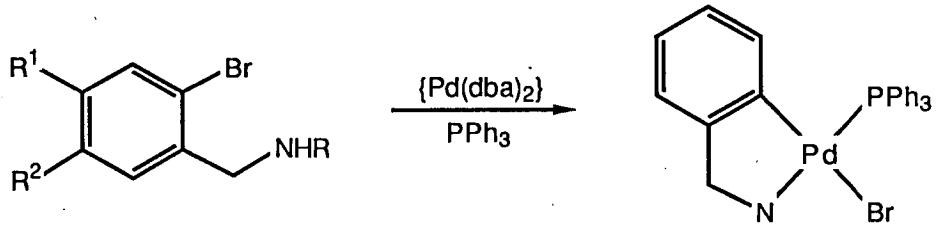
RBr=



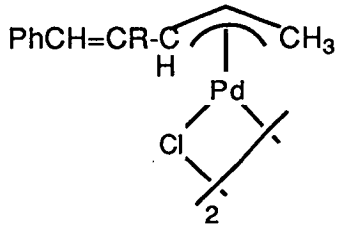


MeI + $\{Pd(CO)(PPh_3)_3\}$ ⟶

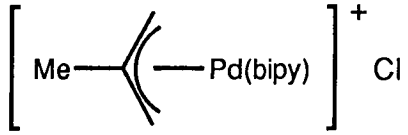




$PhCH{=}CR{-}CH{=}CHCH_2Cl$ $\xrightarrow{\{Pd_2(dba)_3{\cdot}S\}}$



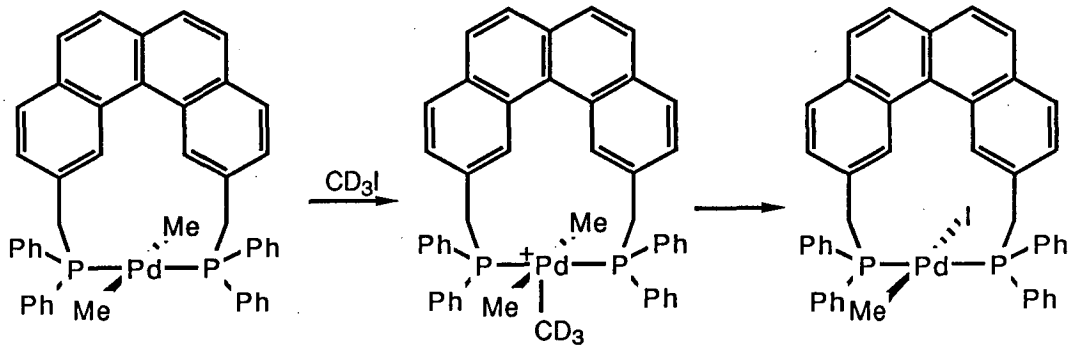
$CH_2{=}CMeCH_2Cl$ $\xrightarrow{\{Pd(bipy)(dba)\}}$



$$\{Pd^{II}R_2(L_2)\} \xrightarrow{RX} \{Pd^{IV}R_3X(L_2)\} \rightarrow \{Pd^{II}RX(L_2)\} + R\text{-}R \qquad 3.1.2\text{-}11$$

(d^8) (d^6) (d^8)

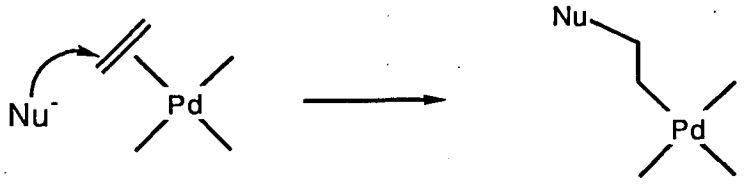
Equation 3.1.2-12[22a]



Both oxidative addition and reductive elimination are very important reactions, since many catalytic and stoichiometric processes involve one, or frequently both, of these steps. A discussion on selected aspects of their importance in organic synthesis can be found in section 3.1.5 and in chapter 5.

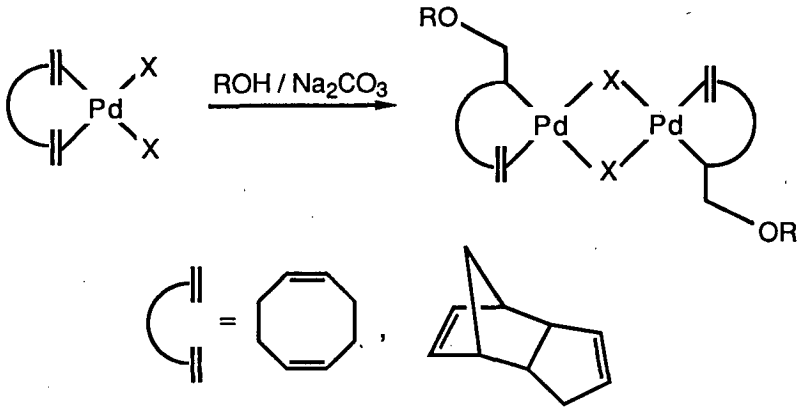
3.1.3 Nucleophilic Addition to Palladium(II)-Olefin Complexes.

A characteristic reaction of many metal-olefin complexes is nucleophilic attack on a coordinated olefin to produce a complex containing a σ-alkylmetal bond, equation 3.1.3-1.



3.1.3-1

Chatt *et al.*[23a] were able to react $PdCl_2$(diene) complexes with alkoxide ions to give complexes in which palladium and the alkoxide ion were added to one double bond, equation 3.1.3-2. This reaction represents the preparation of the first palladium(II) complex containing a metal-carbon σ bond.

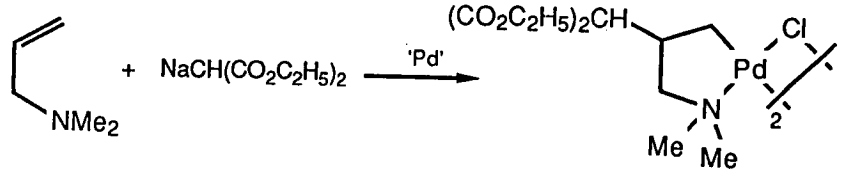


3.1.3-2

R=Me, Et, Pr^n M=Pd,[23a] Pt[23b]

X=Cl, Br

A similar reaction occurs for N,N-dimethylalkylamine,[24] equation 3.1.3-3.

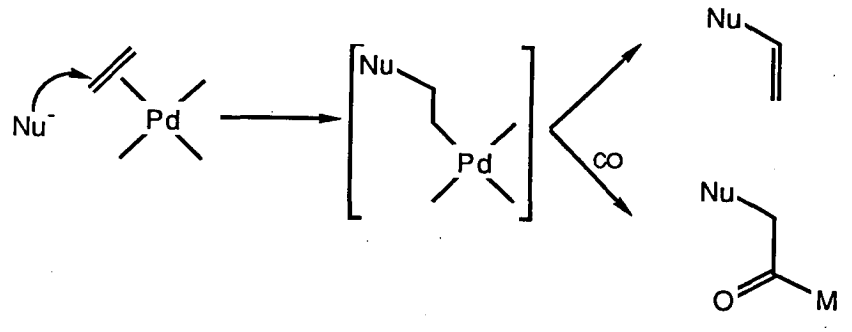


3.1.3-3

The two examples illustrated above involve nucleophilic attack on chelating olefins. The complexes would be expected, due to the chelating nature of the ligands, to exhibit a high degree of stability. Frequently, however, unstable intermediates are formed which undergo spontaneous β-hydrogen elimination, equation 3.1.3-4, or undergo further reactions (*e.g.* insertion reactions) prior to elimination reactions, equation 3.1.3-5

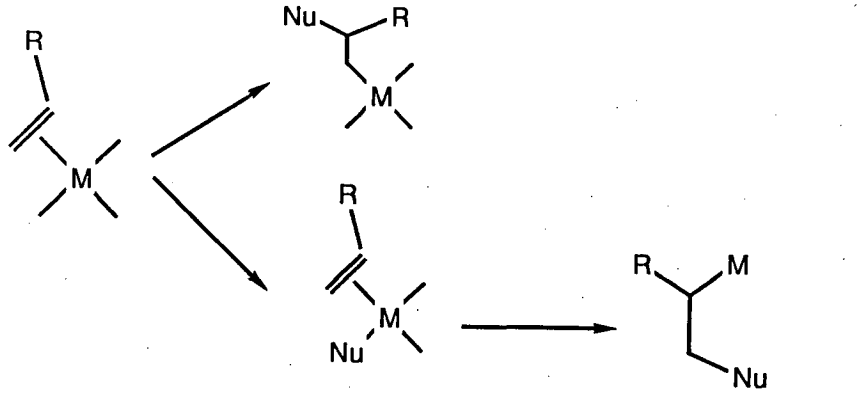
Nucleophilic attack on coordinated olefins, to produce σ-alkylmetal complexes, can proceed *via* two different pathways, which can be distinguished by their relative

regio- and stereochemistry. The prevalent mechanism involves *trans* attack (from the face opposite the metal) by the nucleophile on the olefin, equation 3.1.3-6. In the mechanism, reaction occurs predominantly at the more substituted olefin terminus. In contrast to this, some nucleophiles appear to attack the metal first, followed by insertion of the olefin into the nucleophile-metal bond. This process results in *cis* addition at the less substituted olefin terminus, equation 3.1.3-7.



3.1.3-4

3.1.3-5

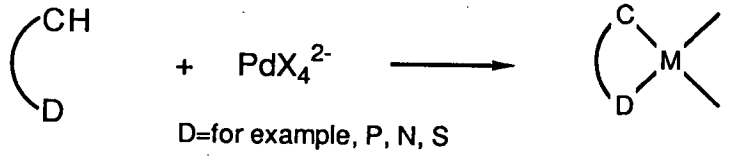


3.1.3-6

3.1.3-7

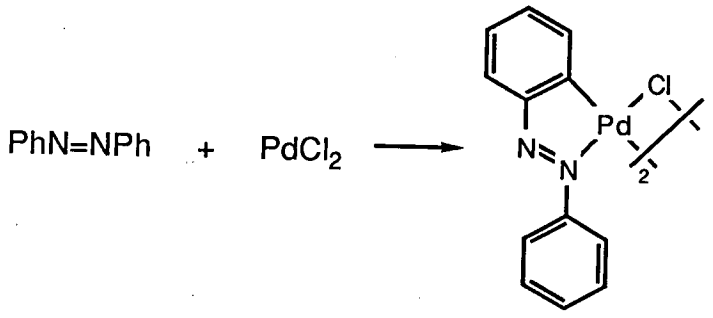
3.1.4 Cyclometallation Reactions

Cyclometallation is the term used to describe the process in which a ligand undergoes intramolecular metallation to form a metal-carbon σ bond as part of a chelate ring, equation 3.1.4-1.



3.1.4-1

For palladium this reaction was first noted in 1965 by Cope and Siekman,[25] equation 3.1.4-2, and was later proposed to proceed by an electrophilic aromatic substitution mechanism.[26] Numerous examples of cyclopalladated complexes have since been reported, and the general reaction has been the subject of several excellent reviews.[27]

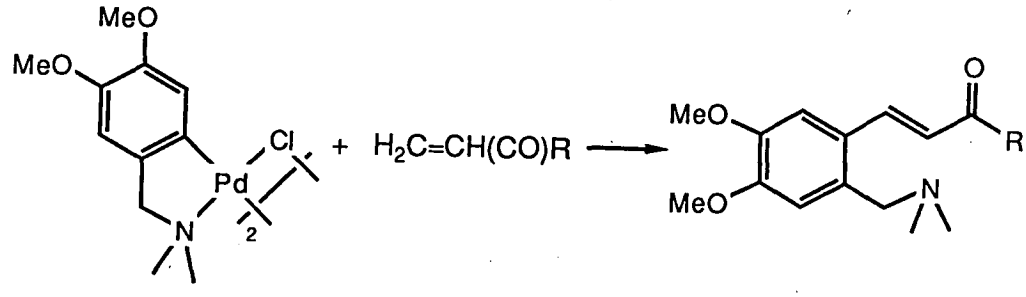


3.1.4-2

Cyclopalladation reactions, involving ligands similar to that discussed earlier, very frequently afford stable, isolable complexes. This stability is a direct result of the chelating nature of the ligand. While examples with donor atoms other than nitrogen are known, nitrogen is the most common for palladium. Also, almost invariably, five membered metallocycles are formed, although smaller and larger ring sizes have been prepared by this reaction.

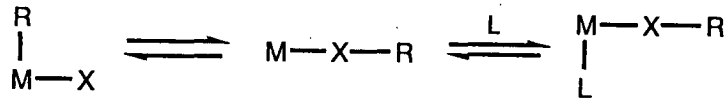
The synthetic usefulness of cyclopalladated complexes is generally a result of subsequent reactions of the complex, *e.g.* insertion reactions, followed by elimination reactions, for example equation 3.1.4-3. Ryabov has recently reviewed the application of cyclopalladated complexes in organic synthesis.[27b]

Equation 3.1.4-2



3.1.5 Insertion Reactions

Insertion reactions involve the combination of an unsaturated ligand (X) with a saturated ligand (R) to form a modified ligand (X-R). Two general classes of insertion reactions are recognised, the first is intramolecular migratory insertions, equation 3.1.5-1 (*e.g.* X=CO, Y=Me), and the second is intermolecular nucleophilic addition, equation 3.1.5-2 (*e.g.* X=C=C, Y=-OMe).



3.1.5-1

3.1.5-2

Intramolecular migratory insertions take place by a combination of X and R while **both** are coordinated to the metal, followed by coordination of a ligand at the vacant site. No net change in formal oxidation state of the metal occurs during a migratory insertion reaction. Intermolecular nucleophilic addition reactions, on the other hand, take place without prior coordination of the nucleophile to the metal, and there may be a change in the formal oxidation state of the metal.

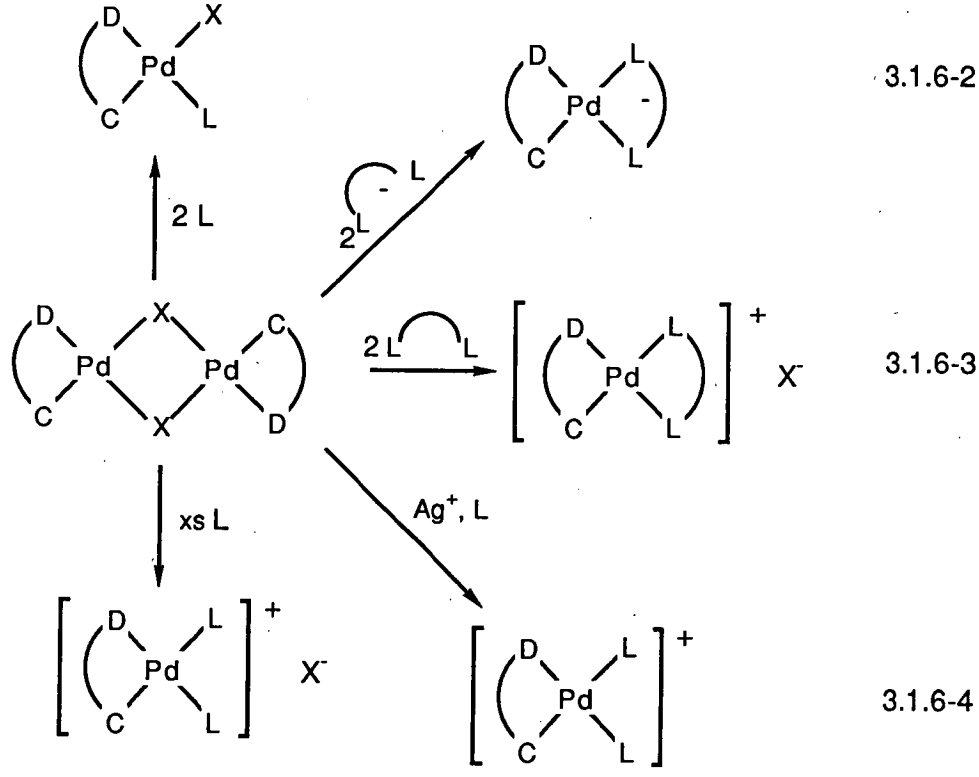
Palladium complexes which contain a σ bonded organic group readily insert small unsaturated molecules, and such reactions have been proposed as key steps in

many catalytic and stoichiometric reactions. Further and more detailed discussions of these reactions can be found elsewhere.[28]

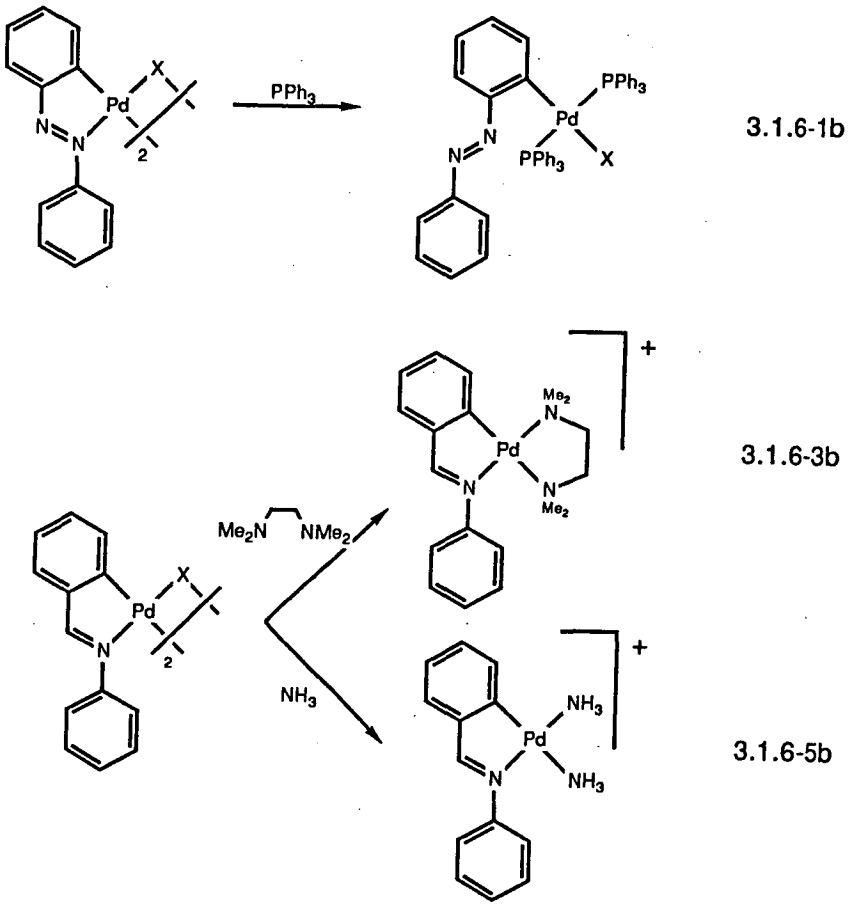
3.1.6 Bridge Splitting Reactions

A major application of halogen bridged cyclometallated palladium(II) complexes is cleavage of the halide bridge with donor ligands to give monomeric complexes. The use of neutral, unidentate donor ligands, *e.g.* L=PPh_3,[29a] or anionic bidentate ligands, *e.g.* Tl(acac),[29a] frequently affords neutral complexes, equations 3.1.6-1 and 3.1.6-2 respectively. The use of neutral, bidentate donor ligands, *e.g.* $H_2NCH_2CH_2NH_2$,[29b] on the other hand, affords cationic complexes, equation 3.1.6-3. Cationic complexes are also prepared by reaction of μ-halogeno-dimers with silver salts (*e.g.* $AgBF_4$ and $AgPF_6$)[29c] in the presence of donor ligands, equation 3.1.6-4, or by reaction with an excess of an unidentate ligand, *e.g.* NH_3,[29c] equation 3.1.6-5.

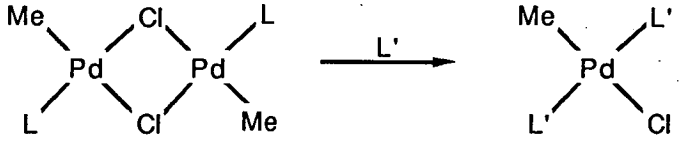
Equation 3.1.6-1



Equation 3.1.6-5



A similar series of reactions also occurs for μ-halogeno-dimers which contain unidentate organo-groups. For example, Hayashi *et al.*[29d] have reported the reaction of $\{PdMe(\mu\text{-}Cl)(L)\}_2$ (L=PEt_3, PMe_2Ph) with donor ligands (L') to yield the monomeric complexes *trans*-$\{PdMeCl(L'_2)\}$, equation 3.1.6-6.



3.1.6-6

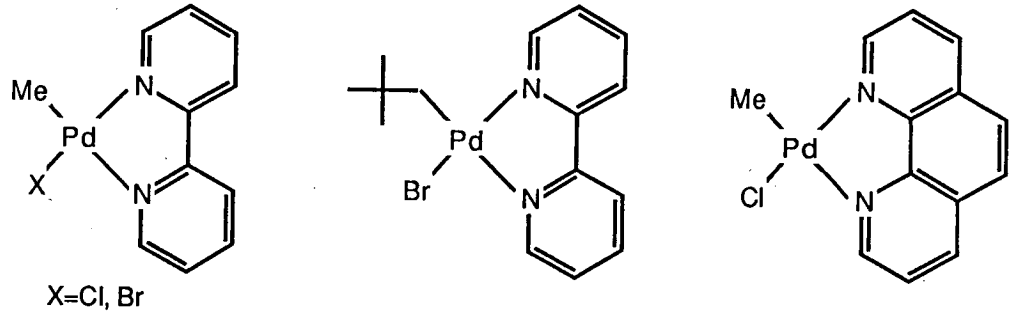
(L=PEt_3, PBu_3, PMe_2Ph)

This general method (*e.g.* equation 3.1.6-6) represents an extremely facile route to monoorganohalopalladium(II) complexes, the full potential of which is yet to be exploited.

Historically, the organometallic chemistry of palladium(II) has been focused on the use of phosphine based ligands, with complexes containing nitrogen donors being generally confined to cyclometallation reactions, *e.g.* equation 3.1.4-1, and intramolecular coordination systems, *e.g.* equation 3.1.3-3.

Despite the synthetic importance of monoorganopalladium(II) species containing nitrogen donor ligands, very few simple monoalkylpalladium(II) complexes containing nitrogen donor ligands are known; reported examples are limited to {PdMeX(bipy)} [X=Cl (preparative procedure not given),[30] I (preparation doubtful, *vide infra*)[31]], {Pd(Me_3CCH_2)Br(bipy)} (reported recently),[22b] and {PdMeCl(2,9-dimethyl-1,10-phenanthroline)}[32] (prepared using organometallic reagents developed during this study, section 3.2 and 3.3.1c), figure 3.1-1.

Figure 3.1-1



Thus, one of the aims of this project was to investigate and develop general synthetic routes to monoalkylhalopalladium(II) complexes with the simplest of alkyl groups, methyl-, and bidentate and tridentate nitrogen donor ancillary ligands.

Two procedures for the preparation of {PdMeX(L_2)} complexes were investigated. The first involved *in situ* preparation, *via* transmetallation reactions, of a 'Pd^{II}MeX' substrate, containing weak donor ligands which could be subsequently replaced with chelating, nitrogen donor ligands, section 3.3.1a. While the second approach involved preparation of {PdMeX(L_2)} complexes from oxidative addition

reactions to either $Pd^0(dba)_n$, or to diorganopalladium(II) complexes, $\{PdMe_2(L_2)\}$, section 3.3.1b.

3.2 PREPARATION AND CHARACTERISATION OF THE DIMERS $\{PdMe(X)(SMe_2)\}_2$.

During the development of routes to N-donor complexes prepared from an *in situ* '$Pd^{II}MeX$' substrate, section 3.3, the halogeno-dimers $\{PdMe(X)(SMe_2)\}_2$ (X=Cl, Br, I) were isolated, and subsequently characterised. Their formation was investigated and may be accomplished by a variety of methods, using MeLi, MeMgI, oxidative addition of MeX, and halide exchange reactions. Characterisation was by near and far infrared, ^1H N.M.R. and mass spectra, microanalysis, and molecular weight determinations in $CHCl_3$ at 37°C. For the chloro-bridged dimer, $\{PdMe(\mu\text{-}Cl)(SMe_2)\}_2$, crystals suitable for crystallographic studies were obtained, and the structure subsequently determined by Dr. A. H. White and colleagues of the University of Western Australia.

3.2.1 Preparative Routes

(a) *via* Transmetallation Reactions.

The complexes $\{PdMe(X)(SMe_2)\}_2$ (X=Cl, Br) were prepared by reaction of the corresponding dihalide *trans*-$\{PdX_2(SMe_2)_2\}$ with one mole equivalent of halide-free (h.f.) methyllithium (~0.4% LiCl), equation 3.2.1-1. Preparation of the analogous iodo-dimer by this method was not attempted due to the instability of *trans*-$\{PdI_2(SMe_2)_2\}$.[33] The desired complex $\{PdMe(I)(SMe_2)\}_2$ was, however, readily prepared by the reaction of MeLi/LiI (prepared according to equation 3.2.1-2) and *trans*-$\{PdCl_2(SMe_2)_2\}$, equation 3.2.1-3 (X=I). The bromo-dimer could also be prepared in this manner using MeLi/LiBr, equation 3.2.1-3 (X=Br), although this method was not preferred as the complex was isolated in lower yield and was

occasionally contaminated with *trans*-{$PdBr_2(SMe_2)_2$} (identified from near and far infrared spectra).[33]

trans-{$PdCl_2(SMe_2)_2$} + MeLi → 1/2 {$PdMe(X)(SMe_2)$}$_2$ 3.2.1-1

X (yield)=Cl (45%), Br (70%)

2 Li + MeI → MeLi + LiI 3.2.1-2

trans-{$PdCL_2(SMe_2)_2$} + 2 MeLi → 1/2 {$PdMe(X)(SMe_2)$}$_2$ 3.2.1-3

X (yield)=Br (~35%), I (85%)

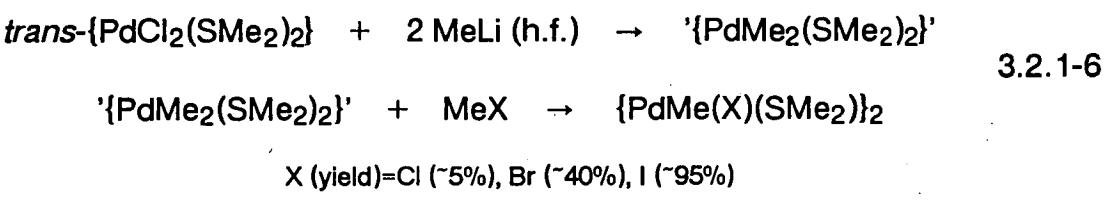
An alternative preparative route to the iodo-dimer was by reaction of MeMgI (prepared according to equation 3.2.1-4) with *trans*-{$PdCl_2(SMe_2)_2$}, equation 3.2.1-5. This method was less useful due to the lower yield obtained, and decreased 'cleanliness' of the reaction.

Mg + MeI → MeMgI 3.2.1-4

trans-{$PdCl_2(SMe_2)_2$} + 2 MeMgI → 1/2 {$PdMe(I)(SMe_2)$}$_2$ 3.2.1-5

(b) *via* Reaction with MeX (X=Cl, Br, I).

The chloro-, bromo- and iodo-dimers were also prepared, *albeit* in lower yield for X=Cl and Br, from the reaction of '$PdMe_2(SMe_2)_2$' with methyl halide (MeX), equation 3.2.1-6. The procedure involved preparation of '$PdMe_2(SMe_2)_2$' from *trans*-{$PdCl_2(SMe_2)_2$} and two mole equivalents of methyllithium (h.f.), step I, followed by addition of MeX (X=Cl, Br, I) at *ca.* -30°C, step II. Work-up of the reaction mixture was identical to that followed for preparations *via* transmetallation reactions.



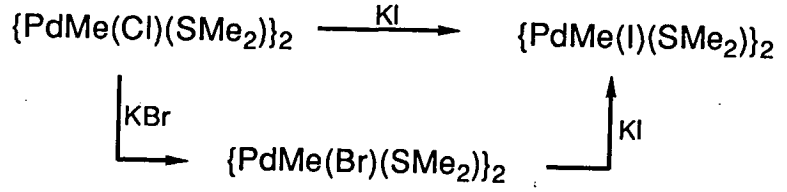
3.2.1-6

This procedure gave poor to moderate yields for the chloro- and bromo-dimers (respectively), but excellent yields for the iodo-dimer. For preparation of the iodo-dimer this is clearly the method of choice.

(c) *via* Halide Exchange Reactions.

A third method developed for the preparation of the bromo- and iodo-dimers was *via* halide exchange reactions with $\{PdMe(Cl)(SMe_2)\}_2$ or $\{PdMe(Br)(SMe_2)\}_2$, equation 3.2.1-7. The procedure involved addition of an aqueous solution of KX (X=Br or I) to a suspension of the chloro-dimer in diethyl ether. Stirring at room temperature, followed by removal of diethyl ether, afforded the desired dimer $\{PdMe(X)(SMe_2)\}_2$ (X=Br or I), in moderate to high yields.

Although this procedure was a convenient route to $\{PdMeX(SMe_2)\}_2$ (X=Br, I), the overall yield for its preparation is limited by the yield obtained for preparation of the reagent dimer. For example, the chloro-dimer is prepared in 45% yield, and if reaction with KI is quantitative then the iodo-dimer is also prepared in only 45% yield. Alternatively, this dimer may be obtained readily in greater than 90% yield from the reaction of '$PdMe_2(SMe_2)_2$' with MeI (see section 3.2.1-b).



3.2.1-7

As the iodo-dimer was prepared in such high yield, it was envisaged that removal of the iodide ion with Ag^+, followed by addition of the required halide ion

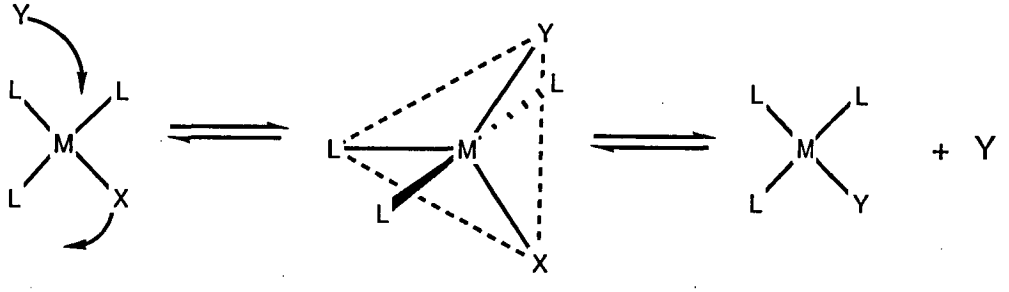
(*i.e.* KCl, KBr) would provide a high yield route to the chloro- and bromo-dimers, equation 3.2.1-8. Reaction sequences identical to those outlined below, in either acetone or acetonitrile solvent, produced the required 'PdMeX' moiety (determined from reactions with nitrogen donor ligands, see section 3.3.1c), but attempts to isolate the dimers failed.

$$\{PdMe(I)(SMe_2)\}_2 \xrightarrow{Ag^+} \text{'}PdMe(SMe_2)\text{'} \xrightarrow{X^-} \{PdMe(X)(SMe_2)\}_2 \qquad 3.2.1\text{-}8$$

Mechanism for Syntheses a, b and c

The mechanism for formation of the bromo- and iodo-dimers *via* halide exchange reactions (section 3.2.1c) is straightforward and most likely proceeds by an associative mechanism, with the formation of a transient five coordinate intermediate,[34] scheme 3.2.1-1.

Scheme 3.2.1-1



Likewise, formation of the halogeno-dimers from the reaction of methylhalides with '$PdMe_2(SMe_2)_2$' is straightforward. The mechanism most likely involves oxidative addition of MeX to '$PdMe_2(SMe_2)_2$', to give a transient Pd(IV) intermediate which, upon warming, reductively eliminates ethane to yield '$PdMeX(SMe_2)_2$', followed by dimerisation to $\{PdMe(X)(SMe_2)\}_2$, equation 3.2.1-9. Repeated attempts without the addition of MeX yields reduced palladium only, with no trace of the chloro-dimer. The decreasing order of yield Cl<Br<I mirrors the expected relative

rates of reaction of the halides *i.e.* RCl<RBr<RI, which is the order commonly found in oxidative addition reactions.[35]

$$\text{'PdMe}_2(\text{SMe}_2)_2\text{'} \xrightarrow{\text{MeX}} \text{'PdMe}_3\text{X}(\text{SMe}_2)_2\text{'} \rightarrow \{\text{PdMe(X)}(\text{SMe}_2)\}_2 \qquad 3.2.1\text{-}9$$

Formation of the chloro- and bromo-dimers from stoichiometric transmetallation reactions, *i.e.* equation 3.2.1-1, can conceivably occur *via* two mechanisms; the first as a direct result of the stoichiometric control of reagents, and the second by redistribution reactions between $Pd^{II}R_2$ and $Pd^{II}X_2$ species.

Previous attempts to prepare monoalkylpalladium(II) complexes *via* stoichiometric control of reagents have failed,[22b] *e.g.* equation 3.2.1-10. This was proposed to be due to the fact that the complexes $\{PdCl_2(L_2)\}$ (L_2=bipy, phosphine ligands) are virtually insoluble in diethyl ether, and as a consequence the alkylating reagent was always in excess in solution during the alkylation.

$$1\ \{PdX_2(L_2)\} + 1\ RLi \not\rightarrow \{PdRX(L_2)\} \qquad 3.2.1\text{-}10$$

X=Cl, L=bipy, R=neopentyl

The complexes *trans*-$\{PdCl_2(SMe_2)_2\}$ (X=Cl, Br), however, exhibit higher solubilities in diethyl ether, and even at -60°C colouration of the solution due to the partial dissolution of the complexes is evident. Further, the order of yield, Cl<Br from this preparative method, may be explained by the qualitative observation that *trans*-$\{PdCl_2(SMe_2)_2\}$ is less soluble than *trans*-$\{PdBr_2(SMe_2)_2\}$.

The alternative mechanism, *i.e. via* symmetrisation reactions, involves alkyl-group transfer from a rapidly formed dimethylpalladium(II) species, probably $\{PdMe_2(SMe_2)_2\}$, to dichloropalladium(II), equation 3.2.1-11. Similar symmetrisation reactions for gold, platinum and palladium have been reported previously.[36]

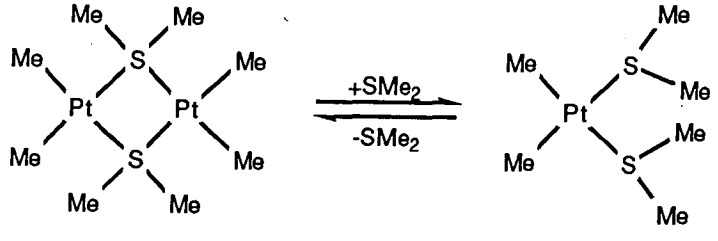
trans-{$PdX_2(SMe_2)_2$} + 2 MeLi (h.f.) → '$PdMe_2(SMe_2)_2$'

3.2.1-11

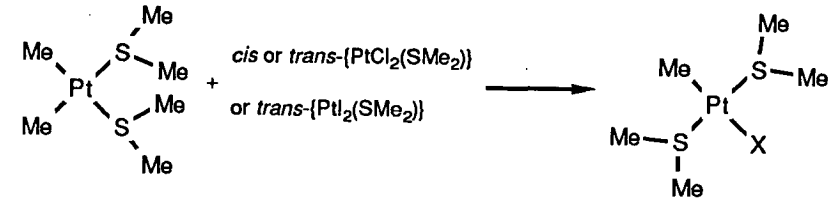
'$PdMe_2(SMe_2)_2$' + *trans*-{$PdX_2(SMe_2)_2$} →→ {$PdMe(X)(SMe_2)$}$_2$

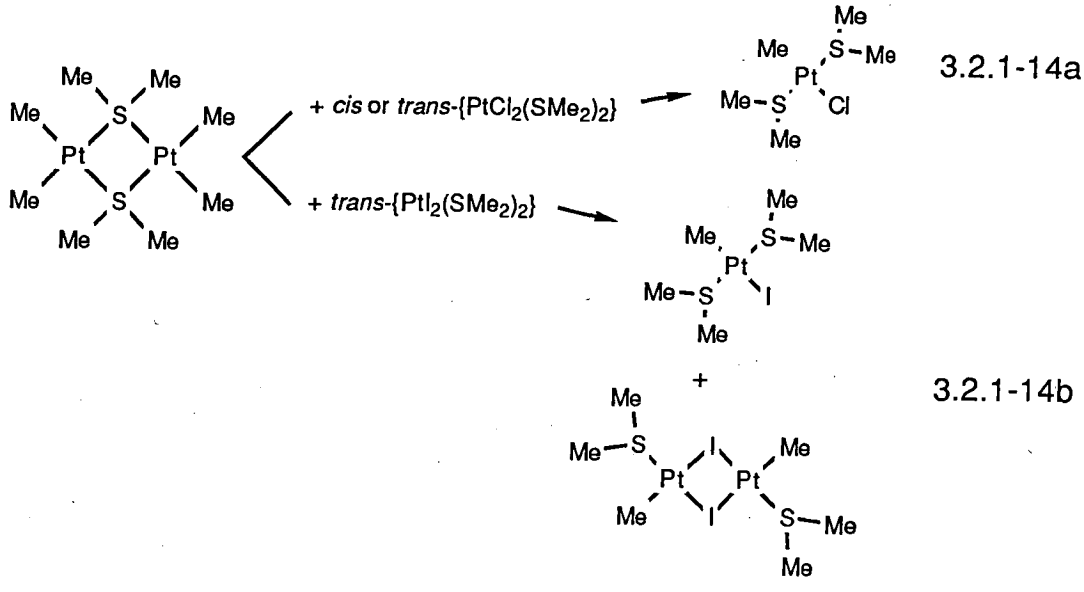
Indeed, reaction of '$PdMe_2(SMe_2)_2$' (prepared from *trans*-{$PdCl_2(SMe_2)_2$} and 2 mole equivalents of MeLi (h.f.)) with one mole equivalent of *trans*-{$PdCl_2(SMe_2)_2$} at -50→ -30°C gave, *albeit* in variable yield (0-20%), {$PdMe(Cl)(SMe_2)$}$_2$. Analogous reactions without addition of *trans*-{$PdCl_2(SMe_2)_2$} consistently gave massive reductive with no trace of the chloro-dimer.

Scott and Puddephatt[36b] have investigated an analogous system with {$PtMe_2(\mu\text{-}SMe_2)$}$_2$. They found that reaction of *cis*-{$PtMe_2(SMe_2)_2$} (formed according to equation 3.2.1-12) with either *cis*- or *trans*-{$PtCl_2(SMe_2)_2$} occurred readily ($T_{1/2}$~20 mins) to give *trans*-{$PtMeCl(SMe_2)_2$}; a similar reaction with *trans*-{$PtI_2(SMe_2)_2$} gave *trans*-{$PtMeI(SMe_2)_2$}, with the reaction complete in 5-10 minutes, equation 3.2.1-13. Further they found that reaction of the dimer {$PtMe_2(\mu\text{-}SMe_2)$}$_2$ with either *cis*- or *trans*-{$PtCl_2(SMe_2)_2$} gave *trans*-{$PtMeCl(SMe_2)_2$} in *ca.* 5 minutes, equation 3.2.1-14a, while reaction of *trans*-{$PtI_2(SMe_2)_2$} occurred even more rapidly to yield *trans*-{$PtMeI(SMe_2)_2$} and the dimer {$PtMe(\mu\text{-}I)(SMe_2)$}$_2$, which could not be isolated, equation 3.2.1-14b.



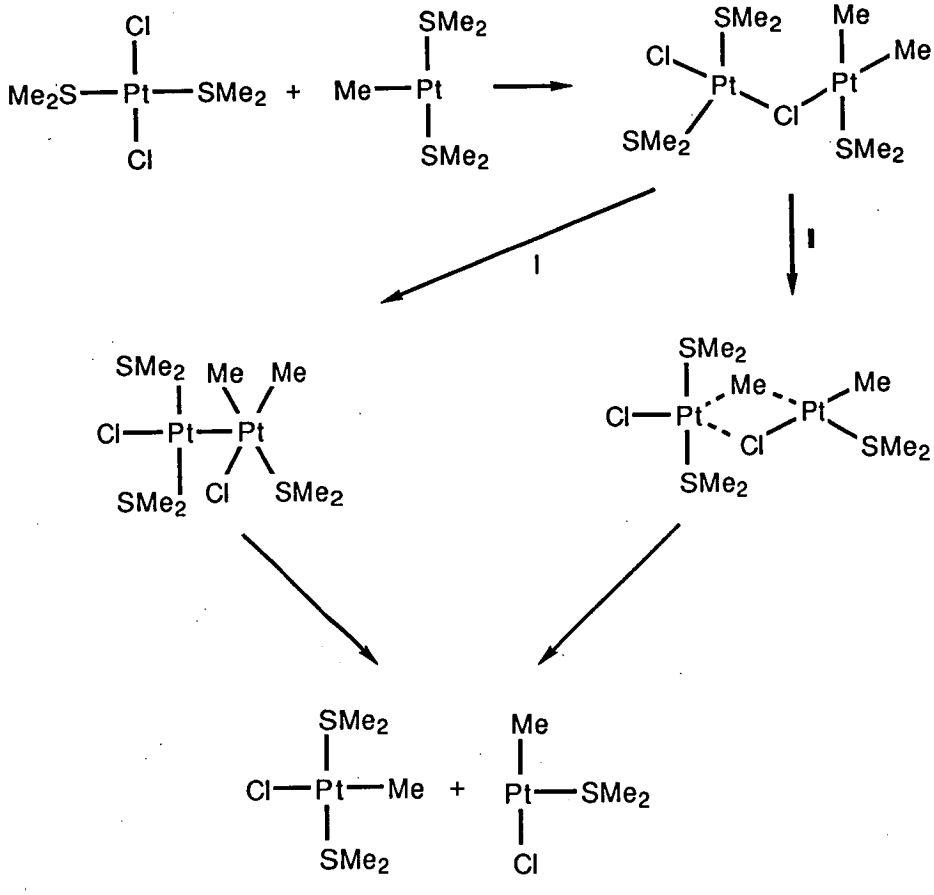
3.2.1-12





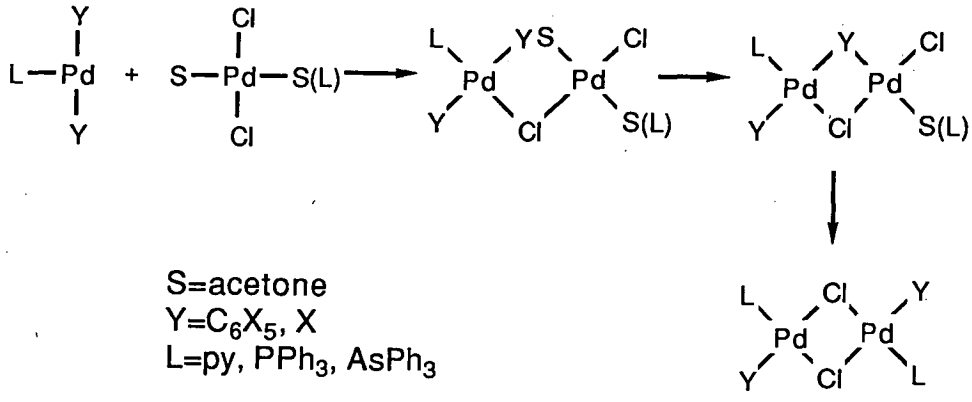
The intermediate species for which methyl for halide exchange occurs, can be formed from two possible mechanisms. The first involves the formation of a cyclic intermediate (*i.e.* S_E2 mechanism), while the second involves a bis-platinum intermediate formed *via* oxidative addition. Scott and Puddephatt have proposed several possible pathways involving both mechanisms outlined above, but their work could not distinguish between them. One possible pathway is outlined below, scheme 3.2.1-2, and involves donation of a lone pair from a chloro-ligand of *trans*-$\{PtCl_2(SMe_2)_2\}$ to the coordinatively unsaturated species '$PtMe_2(SMe_2)$', followed by either oxidative addition-reductive elimination (I) or the S_E2 mechanism (II).[36b]

Scheme 3.2.1-2.



A similar mechanism for the symmetrisation of $PdCl_2$ with $\{PdY_2(L_2)\}$ ($Y=C_6X_5$, X; L=py, PPh_3, $AsPh_3$) in acetone has been reported by Uson *et. al.*[36c] The mechanism was proposed to proceed by initial donation from a chloro-ligand of $PdCl_2S_2$ (S=acetone) to an unsaturated PdY_2L molecule, followed by the S_E2 mechanism, scheme 3.2.1-3.[36c]

Scheme 3.2.1-3



A mechanism analogous to those outlined above can be readily envisaged for the palladium(II) dimers prepared during this study. But, as the yield of the chloro-dimer isolated from the reaction of '$PdMe_2(SMe_2)_2$' with *trans*-$\{PdCl_2(SMe_2)_2\}$ was always < ~50% of that obtained from the stoichiometric reaction between *trans*-$\{PdCl_2(SMe_2)_2\}$ and MeLi (h.f.) the alternative mechanism, *i.e. via* stoichiometric control of reagents, may contribute *ca.* 50% of the overall yield. Hence, preparation of the chloro- and bromo-dimers from stoichiometric reactions can best be described by a combination of symmetrisation reactions together with stoichiometric control of reagents.

The reaction of *trans*-$\{PdCl_2(SMe_2)_2\}$ with two mole equivalents of either MeLi/LiI or MeLi/LiBr to form $\{PdMe(I)(SMe_2)\}_2$ or $\{PdMe(Br)(SMe_2)\}_2$, respectively, cannot be readily explained by any of the mechanisms described above; similar reactions with halide-free methyllithium yield palladium metal only. The reaction with MeLi/LiI can be understood, however, if the reaction between methyliodide and lithium proceeds according to equation 3.2.1-15. Thus, methylation of *trans*-$\{PdCl_2(SMe_2)_2\}$ with MeLi/LiI gives '$PdMe_2(SMe_2)_2$' which subsequently undergoes oxidative addition of MeI, followed by reductive elimination of ethane to yield $\{PdMe(I)(SMe_2)\}_2$, equation 3.2.1-16.

$$Li + MeI \longrightarrow MeLi + Li + MeI + LiI \qquad 3.2.1\text{-}15$$

(unbalanced)

$$2\ MeLi / LiI + \textit{trans}\text{-}\{PdCl_2(SMe_2)_2\} \longrightarrow \text{'}PdMe_2(SMe_2)_2\text{'}$$

$$\downarrow + MeI \qquad 3.2.1\text{-}16$$

$$\{PdMe(I)(SMe_2)\}_2$$

To confirm this *trans*-$\{PdCl_2(SMe_2)_2\}$ was reacted firstly with MeLi (h.f.) which had been doped with LiI, and, secondly with MeLi (h.f.) doped with MeI. The former reaction, upon work-up, gave palladium metal only, while the latter afforded the iodo-dimer. Lashanizadehgan *et. al.*[37] have reported a similar reaction where attempts to methylate $\{PtCl_2(SMe_2)_2\}$ with MeLi/LiI (prepared according to equation 3.2.1-15) gave the Pt(IV) dimer, $\{PtMe_4(\mu\text{-}SMe_2)\}_2$, instead of the expected Pt(II) dimer, $\{PtMe_2(\mu\text{-}SMe_2)\}_2$. The reaction was proposed to involve oxidative addition of MeI to the dimethylplatinum(II) intermediate, followed by metathetical displacement of iodide with methyllithium.

The mechanism of formation of the bromo-dimer from *trans*-$\{PdCl_2(SMe_2)_2\}$ and MeLi/LiBr (obtained commercially) is essentially unknown. An oxidative addition-reductive elimination sequence is unlikely as MeBr is a gas at room temperature (b.pt. 3.56°C).[38] However, MeBr is freely soluble in diethyl ether,[38] and indeed 2.0M solutions in diethyl ether can be obtained commercially; it is thus interesting to speculate whether commercially obtained MeLi/LiBr (in diethyl ether) contains residual MeBr.

3.2.2 Characterisation

The halogeno-dimers prepared above were characterised by microanalysis, ^1H N.M.R, vibrational and mass spectroscopy, and molecular weight determinations.

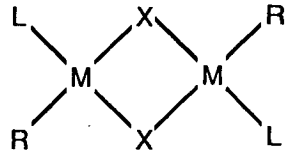
Microanalysis (C,H) and ^1H N.M.R. spectra were consistent with the empirical formula 'PdMe(X)(SMe_2)', *e.g.* the ^1H N.M.R. spectra displayed only two peaks in 2(SMe_2) :1(PdMe) ratio. The dimeric nature of the complexes was confirmed by molecular weight determinations in chloroform at 37°C.

While the three halogeno-dimers displayed very similar ^1H N.M.R. and near infrared spectra, their mass spectra readily differentiated between them. Decomposition of the dimers in the mass spectrometer produced the characteristic fragments shown in equation 3.2.2-1. For example, the bromo-dimer shows in its mass spectrum, isotopic ratios of $Me^{79,81}Br$, $^{79,81}Br$, $H^{79,81}Br$, while the chloro- and iodo-dimers show MeCl, Cl, HCl (in isotopic ratio) and MeI, I, HI respectively.

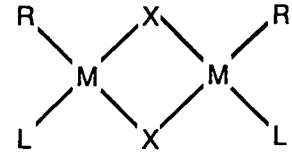
$$\{PdMe(X)(SMe_2)\}_2 \rightarrow MeX + X + HX \ (+ \ SMe_2) \qquad 3.2.2\text{-}1$$

Structurally, the dimers may contain either bridging halide (X), or bridging thioether (L) groups, and exhibit either the *cis* or *trans* configuration, figure 3.2.2-1.

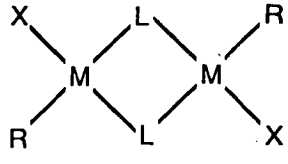
Figure 3.2.2-1



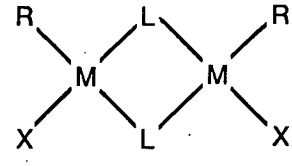
(a) *trans*, μ-halide



(b) *cis*, μ-halide



(c) *trans*, μ-thioether



(d) *cis*, μ-thioether

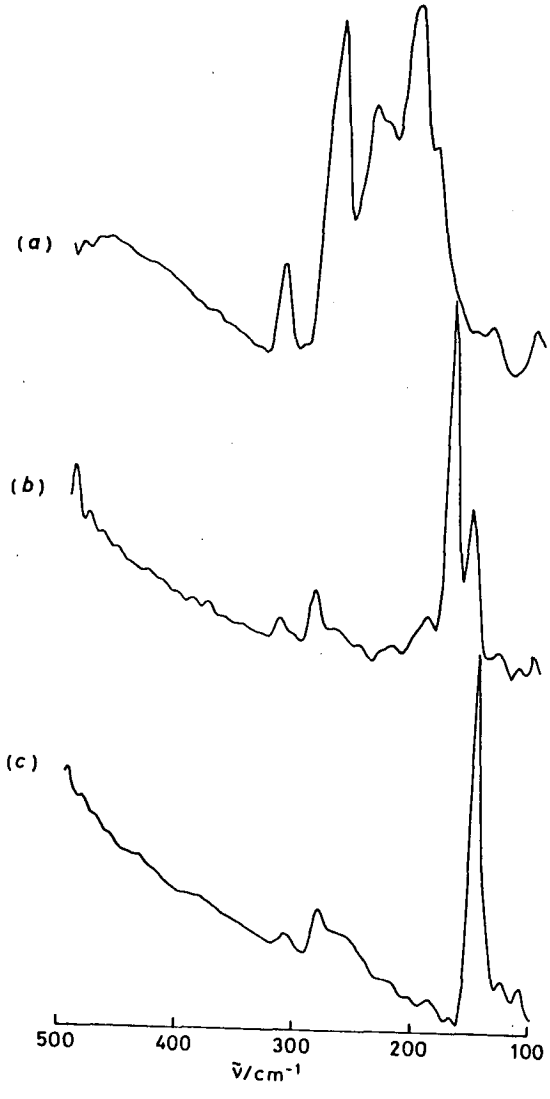
For the closely related inorganic dimers (R=X=halide) differing behaviour is observed between palladium and its congener platinum. For palladium the inorganic dimers are known to have the *trans* configuration with bridging **halogeno** groups, figure 3.2.2-1a (R=X). This was established from vibrational and ^{1}H N.M.R. spectroscopic studies, $\{PdX(\mu\text{-}X)(SMe_2)\}$ (X=Cl, Br),[33,39] and an X-ray crystallographic study for $\{PdBr(\mu\text{-}Br)(SMe_2)\}_2$.[40] In contrast, vibrational spectra indicate that for platinum the complexes contain bridging **thioether** groups, $\{PtX_2(\mu\text{-}SMe_2\}_2$ (X=Cl, Br),[40a,41] figure 3.2.2-1c, which has been shown crystallographically for $\{PtBr_2(\mu\text{-}SEt_2)\}_2$.[40] However, spectroscopic studies (^{1}H N.M.R. and vibrational) indicate that $\{PtI(\mu\text{-}I)(SMe_2)\}_2$ contains bridging iodo-groups, with either the *cis* or *trans* configuration,[41] figure 3.2.2-1a,b.

Methylmetal complexes of formula $\{MMe(X)(SMe_2)\}_2$ (M=Pt, Pd; X=Cl, Br, I) may also exhibit similar structural isomerism. Indeed, ^{1}H N.M.R. spectroscopic studies revealed that $\{PtMe(\mu\text{-}I)(SMe_2)\}_2$ contained bridging iodo-groups,[36b] with the molecule exhibiting both the *cis* and *trans* configuration. Assignment of structure was possible from the observed multiplicity of the SMe_2 resonance. For SMe_2 bridging the platinum centres, coupling with ^{195}Pt would result in 5 resonances in 1:8:18:8:1 ratio, whereas SMe_2 in a terminal position would give 3 resonances in 1:4:1 ratio. Palladium, however, does not contain an isotope which displays observable Pd-^{1}H coupling, and thus elucidation of bridging or terminal SMe_2 in $\{PdMe(X)(SMe_2)\}_2$ on similar arguments is not possible.

The dimers do, however, display radically different far infrared spectra (500-100 cm^{-1}), as expected, since this region contains palladium-halogen stretching frequencies. Adams and Chandler[42] have reported palladium-halide stretching frequencies for complexes $\{PdX(\mu\text{-}X)(L)\}_2$ (X=Cl, Br; L=PCl_3, $P(OEt)_3$, PR_3, AsR_3, SR_2, SeR_2, TeR_2, py, olefins) and give values of 370-345 (285-265) for **terminal** chlorides (bromides), and 310-300 (200-185) and 280-250 (200-165) for **bridging** chlorides (bromides); and Goggin *et. al.*[33] have reported fully assigned spectra for the complexes $\{PdX(\mu\text{-}X)(SMe_2)\}_2$ (X=Cl, Br).

The far infrared spectra of the complexes $\{PdMe(X)(SMe_2)\}_2$ (X=Cl, Br, I) are shown in figure 3.2.2-2, and are presented in table 3.2.2-1 along with reported assignments for the most closely related inorganic complexes $\{PdX(\mu\text{-}X)(SMe_2)\}_2$ (X=Cl, Br).

Figure 3.2.2-2 Far-i.r. spectra of $\{PdMe(X)(SMe_2)\}_2$: X=Cl (a), Br (b), or I (c)



The first important feature to note about the spectra is that they show only one absorption, of weak intensity, above 300 cm^{-1} (at 319 (X=Cl), 319 (X=Br), and 309 cm^{-1} (X=I)). This has been assigned as $\upsilon(Pd\text{-}S)_{terminal}$ by comparison with $\{PdX(\mu\text{-}x)(SMe_2)\}_2$ (which has $\upsilon(Pd\text{-}X)_{terminal}$ at 340 (X=Cl) and 336 cm^{-1} (X=Br)).[33b]

Table 3.2.2-1. Spectra (500-100 cm-1) of [{PdX(μ-X)(SMe_2)}$_2$][a] and [{PdMeX(SMe_2)}$_2$]][b]

	[{PdCl(μ-Cl)(SMe_2)}$_2$]	[{PdMe(μ-Cl)(SMe_2)}$_2$]	[{PdBr(μ-Br)(SMe_2)}$_2$]	[{PdMeBr(SMe_2)}$_2$][c]	[{PdMeI(SMe_2)}$_2$][d]
Pd-S str. (terminal)	340ms	319w	336s	319w	309w
Pd-X str. (terminal)	360s		274s		
Pd-X str. (bridging)	308ms[e]	275vs	223s[e]	175vs	150vs[h]
Pd-X str. (bridging)	282s[f]	244s.br[g]	195ms[f]	157m	
SC_2 def.		~285w (sh)	295ms	288mw	280mw
CSPd def.	209m, br	211vs[i]	185 (sh)	195m	188w, br
Skeletal and lattice modes	151 (sh) 148ms 132wm	154vw 141vw 105vw	124 (sh) 119m 109vw (sh)	134w 119vw 105w	126w 111w

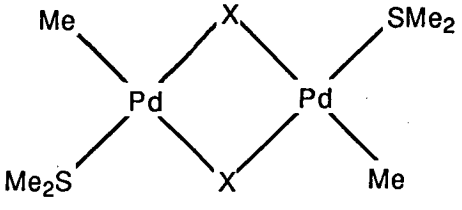
[a] From ref. 33,39 as mulls in mixtures of Nujol and vaseline. [b] This work, as powdered polyethylene discs. [f] Very weak, broad absorptions at ~273, ~252, and ~224 cm^{-1}.
[d] Weak, very broad absorption at 270-240 cm^{-1}. [e] *trans* to S. [f] *trans* to X. [g] Shoulder at ~235 cm^{-1}. [h] Unsymmetrical broader base at low frequency. [i] Shoulder at 193w cm^{-1}.

Secondly, the major absorption at 290-240 cm^{-1} for the chloro-dimer, 180-150 cm^{-1} for the bromo-dimer, and 150 cm^{-1} for the iodo-dimer are lower than expected for $\upsilon(Pd\text{-}X)_{terminal}$ frequencies, *e.g.* $\upsilon(Pd\text{-}Cl)_{terminal}$=370-345 cm^{-1},[42] and hence are readily assigned as $\upsilon(Pd\text{-}X)$ bridging; similar values for $\upsilon(Pd\text{-}X)_{bridging}$ are obtained for the closely related inorganic analogues $\{PdX(\mu\text{-}X)(SMe_2)\}_2$ (X=Cl, Br).

Finally, with this assignment of $\upsilon(Pd\text{-}X)_{bridging}$, the ratios $\upsilon(Pd\text{-}X)/\upsilon(Pd\text{-}Cl)$ ~0.64(X=Br) and ~0.57 (X=I) are as expected,[43] and, consistent with observations of Adams and Chandler for $\{PdX(\mu\text{-}X)(L)\}_2$,[42] the $\upsilon(Pd\text{-}X)_{bridging}$ absorption at higher frequency is stronger and sharper than the $\upsilon(Pd\text{-}X)_{bridging}$ absorption at lower frequency. This is clearly seen for the chloro- and bromo-dimers, but is less apparent for the iodo-dimer. Although, the $\upsilon(Pd\text{-}I)_{bridging}$ absorption is asymmetric with a broader base at lower frequency, suggesting that a second, weaker $\upsilon(Pd\text{-}I)_{bridging}$ absorption is unresolved.

The three dimers are thus assigned as having bridging halogeno-groups with the *trans* configuration, figure 3.2.2-3.

Figure 3.2.2-3.

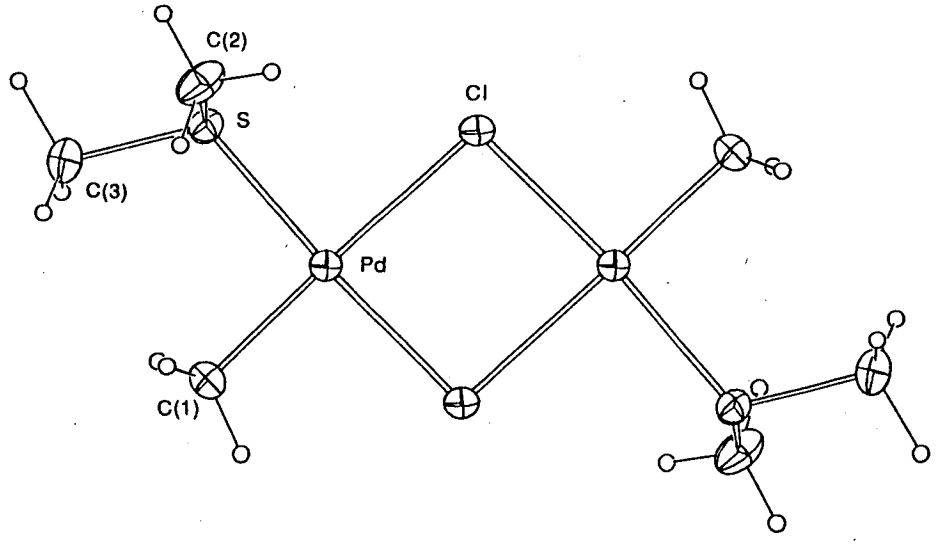


3.2.3 Solid State Structure of $\{PdMe(\mu\text{-}Cl)(SMe_2)\}_2$

To firmly establish structures of the dimers, crystals of $\{PdMe(\mu\text{-}Cl)(SMe_2)\}_2$ were obtained by dissolution of the complex in acetone and slow vapour diffusion of diethyl ether at -20°C, over 48 hours in a sealed chamber.

Molecules of $\{PdMe(\mu\text{-}Cl)(SMe_2)\}_2$ possess a planar skeleton with two chloro-bridged square planar palladium atoms and terminal thioether and methyl ligands in the *trans* configuration, with a centre of symmetry,.figure 3.2.3-1. Angles at each palladium atom are in the range 87.42(4)-93.6(1)°, and the maximum deviation (0.077 Å) from the $PdCl_2SC$ mean plane is observed for the carbon atom C(1). The Pd_2Cl_2 moiety is almost symmetrical, with Pd-Cl distances differing by 0.14 Å.

Figure 3.2.3-1.



As observed for the closely related inorganic bromo-analogue $\{PdBr(\mu\text{-}Br)(SMe_2)\}_2$,[40a] the S-C bonds are not symmetrically related to the plane of the molecule; one bond lies close to the plane (deviation - 0.240Å), while the other is in a plane almost perpendicular to it (deviation 1.658Å).

Bond lengths and angles for $\{PdMe(\mu\text{-}Cl)(SMe_2)\}_2$ are given in table 3.2.3-1.

Table 3.2.3-1. Non-hydrogen Atom Molecular Geometry for trans [{PdMe(μ-Cl)(SMe_2)}$_2$]; Distances in Å, Angles in °: Primed Atoms are Generated by the Inversion Centre at the Centre of the Dimer*

Pd-C(1)	2.016(4)	Pd-S	2.265(1)
Pd-Cl	2.358(1)	S-C(2)	1.792(4)
Pd-Cl	2.498(1)	S-C(3)	1.799(4)
C(1)-Pd-Cl	90.9(1)	Pd-Cl-Pd	92.58(4)
C(1)-Pd-CL	177.3(1)	C(2)-S-Pd	104.5(2)
C(1)-Pd-S	93.6(1)	C(3)-S-Pd	116.2(2)
Cl-Pd-Cl	87.42(4)	C(2)-S-C(3)	99.3(2)
Cl-Pd-S	175.20(3)		
Cl-Pd-S	88.16(4)		

*Atom deviations from the mean plane defined by $PdCl_2SC(1)$ are Pd, 0.004; Cl,-0.033; Cl, 0.005; C(1), 0.077; C(2), 1.658; C(3), -0.240 Å; the plane is given by $0.6179X - 0.4979Y + 0.3738Z = 0014$ (standard significance index for coplanarity χ^2=2649) and the right-hand orthogonal Å frame (*X*,*Y*,*Z*) has *X* parallel to *a*, *Z* in the *ac* plane.

3.3 PREPARATION of MONOMETHYLPALLADIUM(II) COMPLEXES, {PdMeX(L_2)}.

Prior to this study, known examples of monoalkylhalopalladium(II) complexes containing chelating nitrogen donor ligands were limited to {PdMeCl(bipy)},[30] {PdMeI(bipy)},[31] and {Pd(Me_3CCH_2)Br(bipy)}.[22b] All of these complexes, except for {PdMeCl(bipy)} (for which no preparative method was given), were prepared by the reaction of an alkylhalide with the corresponding diorganopalladium(II) complex, equation 3.3-1.

$$\{PdR_2(bipy)\} + R'X \rightarrow \{PdRX(bipy)\} \qquad 3.3\text{-}1$$

(i) R=Me, R'X=C_3F_7I[31]

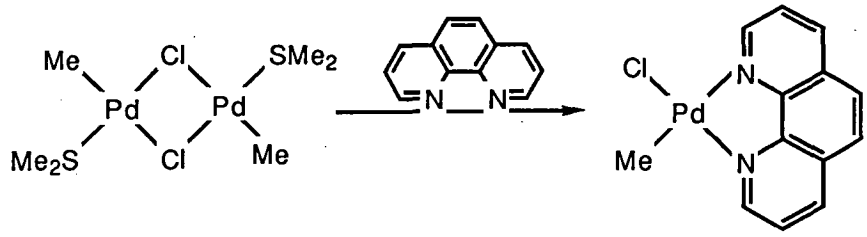
(ii) R=Me_3CCH_2, R'X=$PhCH_2Br$[22b]

The complex {PdMeI(bipy)} ((i) above) was isolated, along with {Pd(C_3F_7)Me(bipy)}, as a byproduct from the reaction of {$PdMe_2$(bipy)} with C_3F_7I. While the diorganopalladium(II) product {Pd(C_3F_7)(Me)(bipy)} was isolated pure, Maitlis and Stone[31] reported that the second product decomposed on purification, contained iodine but no fluorine, and that microanalysis is consistent with {PdMeI(bipy)}, although the authors are uncertain of this formulation.[31] The preparation of {PdMeI(bipy)} in this case does appear doubtful, as preparation of {PdMeI(bipy)} during this study gave a complex which did not display the instability reported by Maitlis and Stone (*vide infra*).

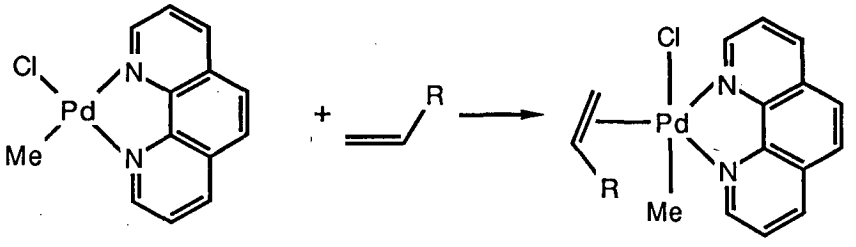
More recently, De Renzi *et al.*[32] have reported the preparation of {PdMeCl(2,9-Me_2-phen)} (2,9-Me_2-phen=2,9-dimethyl-1,10-phenanthroline) and the subsequent preparation of the five coordinate complexes {PdMeCl(2,9-Me_2-phen)(olefin)}. Preparation of {PdMeCl(2,9-Me_2-phen)} was accomplished by reaction of {PdMe(μ-Cl)(SMe_2)}$_2$, prepared and reported[44] during this study (section 3.2), with 2,9-Me_2-phen, *via* a bridge-splitting reaction (section 3.1.6), equation 3.3-2. Treatment of the complex with ethylene or α-olefins afforded the 1:1 adducts {PdMeCl(2,9-Me_2-phen)(olefin)}, equation 3.3-3, for which trigonal bipyramidal structures were proposed[32] (assigned from ^{1}H N.M.R. spectral studies and by comparison with analogous Pt(II) complexes).

A major aim of this project has been the development of general synthetic routes to mono- and dimethylpalladium(II) complexes containing N-donor ligands. For the preparation of monomethylpalladium(II) complexes this was initially investigated using transmetallation reactions (section 3.3.1a), and oxidative addition reactions (section 3.3.1b). Later, synthesis of the bridging halogeno-dimers

{PdMe(μ-X)(SMe_2)} provided a third route to these complexes (section 3.3.1c). Bridge-splitting reactions with {PdMe(μ-X)(SMe_2)}$_2$ proved to be an extremely facile synthetic pathway to {PdMeX(L_2)} complexes for a variety of ligands.



3.3-2



3.3-3

3.3.1 Preparative Procedures

(a) *via* Transmetallation Reactions.

As discussed earlier (section 3.2.1), previous attempts to prepare monoalkylhalopalladium(II) complexes from the stoichiometric reaction of an organolithium or organomagnesium reagent have failed, equation 3.3.1-1, with the diorganopalladium(II) product formed instead, together with much unconverted starting material, equation 3.3.1-2. This is assumed to be due to the extremely low solubility of the complexes {$PdCl_2(L_2)$} in diethyl ether.[22b]

Similarly, the complexes {$PdX_2(L_2)$} (X=halide; L_2=bidentate N-donor ligands used in this study) displayed extremely low solubility in diethyl ether and direct alkylation of these complexes was not attempted, but rather an approach similar to that described in chapter 2 was employed. This involved methylation of *trans*-{$PdCl_2(SMe_2)_2$} at low temperature to form a 'PdMeX' substrate, most likely

$\{PdMeX(SMe_2)_2\}$, which was reacted *in situ* with ligands (L_2) to give, *via* displacement of the weak unidentate ligand SMe_2, the complexes $\{PdMeX(L_2)\}$ (X=halide; L_2=chelating N-donor ligand), equation 3.3.1-3.

$$\{PdCl_2(L_2)\} + RM \not\rightarrow 2\,\{PdRCl(L_2)\} \qquad 3.3.1\text{-}1$$

$$\rightarrow \{PdR_2(L_2)\} + \{PdCl_2(L_2)\} \qquad 3.3.1\text{-}2$$

L_2=bipy, dppe ; L=PMe_2Ph

$$trans\text{-}\{PdCl_2(SMe_2)_2\} + MeM \xrightarrow{L_2} \{PdMeX(L_2)\} \qquad 3.3.1\text{-}3$$

Initially, use of methylmagnesiumiodide (MeMgI) as the alkylating reagent was investigated. Reaction of MeMgI with *trans*-$\{PdCl_2(SMe_2)_2\}$, according to equation 3.3.1-3, gave, upon addition of ligands (L_2) and work-up, the complexes $\{PdMeI(L_2)\}$ in low to moderate yield. The isolation of methyliodo-complexes, *i.e.* $\{PdMeI(L_2)\}$, from a dichloro- starting material, *trans*-$\{PdCl_2(SMe_2)_2\}$, is as expected, and results from metathetical displacement of the chloro-ligand(s) in *trans*-$\{PdCl_2(SMe_2)_2\}$ or $\{PdMeCl(L_2)\}$ with the iodo-ligand in MgI_2. The use of MeMgI, however, was not entirely satisfactory, owing to low yields and difficulties encountered in isolating pure samples.

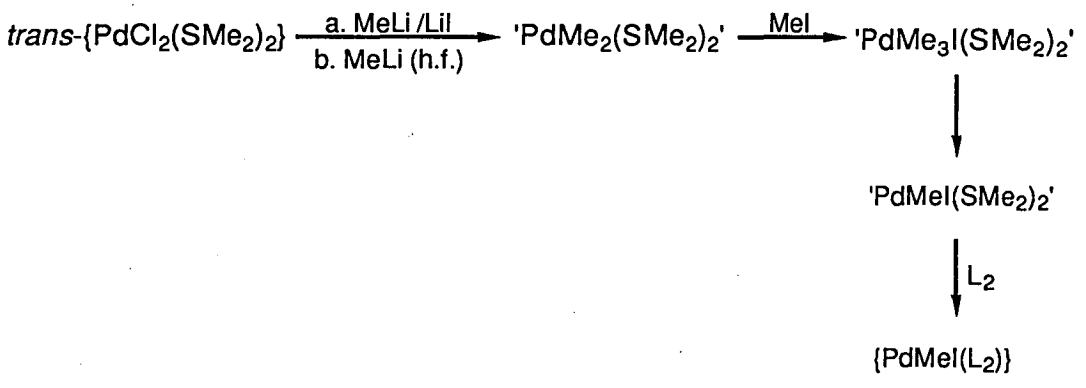
During the development of routes to dimethylpalladium(II) complexes (chapter 2) it was noted that methylation of *trans*-$\{PdCl_2(SMe_2)_2\}$ with MeLi/LiI (prepared according to equation 3.3.1-4), followed by addition of ligands (L_2) afforded the unexpected products $\{PdMeI(L_2)\}$, in moderate to high yield, equation 3.3.1-5.

$$MeI + 2\,Li \rightarrow MeLi + LiI \qquad 3.3.1\text{-}4$$

$$2\,MeLi/LiI + trans\text{-}\{PdCl_2(SMe_2)_2\} \not\rightarrow \{PdMe_2(L_2)\} \rightarrow \{PdMeI(L_2)\} \qquad 3.3.1\text{-}5$$

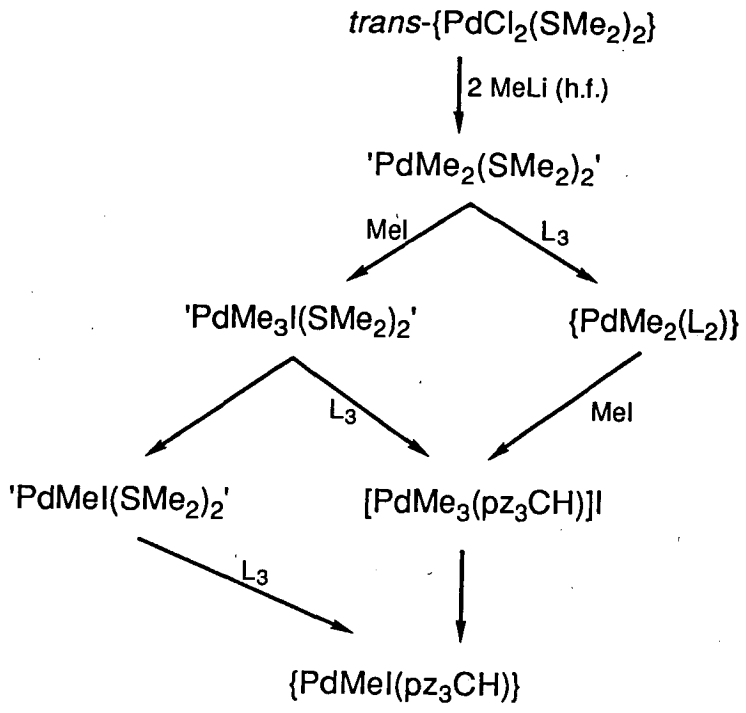
The mechanism for this reaction is most likely very similar to that proposed for the preparation of the iodo-dimer (section 3.2.1), *i.e.* oxidative addition of MeI (present in the MeLi solution) to the '$PdMe_2(SMe_2)_2$' species formed, followed by reductive elimination of ethane, and complexation with L_2, scheme 3.3.1-1 (route a). Indeed, reaction of *trans*-$\{PdCl_2(SMe_2)_2\}$ with 2 mole equivalents of halide-free MeLi, followed by addition of MeI (at -50°C) and ligands (at -20°C) afforded the desired complexes $\{PdMeI(L_2)\}$, scheme 3.3.1-1 (route b); reactions without the addition of MeI gave the complexes $\{PdMe_2(L_2)\}$.

Scheme 3.3.1-1.



A reaction sequence similar to that above, but with the addition of the tridentate ligand pz_3CH (at -40°C), gave a mixture of $[Pd^{IV}Me_3(pz_3CH)]I$ (see chapter 5) and $\{PdMeI(pz_3CH)\}$. Two reaction sequences, both of which involve a Pd(IV) complex can be envisaged. The first involves oxidative addition of MeI to '$PdMe_2(SMe_2)_2$', followed by complexation with pz_3CH, while the second involves complexation of '$PdMe_2(SMe_2)_2$' with pz_3CH, followed by oxidative addition of MeI, scheme 3.3.1-2.

Scheme 3.3.1-2.



A similar mechanism most likely occurs for the preparation of methyliodopalladium(II) complexes with chelating bidentate N-donor ligands. Although in this instance, transient Pd(IV) complexes are formed which reductively eliminate ethane readily to form the complexes {PdMeI(L_2)}.

The preparation of {PdMeI(L_2)} complexes from the reaction of *trans*-{$PdCl_2(SMe_2)_2$} with either MeLi/LiI or MeLi(h.f.)/MeI does, however, have several disadvantages. Firstly, the reaction sequence works well only for ligands which are soluble in diethyl ether at *ca.* -20°C, which is essentially only pyrazole and some pyridine based ligands. Secondly, ligands which have the potential to form stable Pd(IV) complexes, in particular tridentate ligands, may give Pd(IV)/Pd(II) mixtures, and finally the ligands used must be insensitive towards methyllithium, *e.g.* methane bridged ligands such as py_2CH_2 compared with alcohols or ketones such as py_2CO.

(b) *via* Oxidative Addition.

The preparation of monoorganohalopalladium(II) complexes *via* oxidative addition was investigated using two approaches. The first involved oxidative addition to Pd(0), while the second involved oxidative addition to Pd(II), followed by reductive elimination from the transient Pd(IV) complex formed.

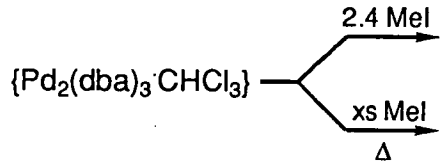
(i) Oxidative Addition to Pd(0)

This method involves oxidative addition of MeI to a Pd(0) substrate, followed by addition of a ligand (L_2) to form the desired complex {PdMeI(L_2)}, equation 3.3.1-6.

$$Pd(0) + MeI \rightarrow \text{'PdMeI'} \xrightarrow{L_2} \{PdMeI(L_2)\} \qquad 3.3.1\text{-}6$$

Traditionally, such approaches have been concentrated on the use of palladium-phosphine substrates, very frequently $Pd(PPh_3)_4$. Clearly, this type of reagent would not be suitable for the weak donors used in this study, *e.g.* pz_2CH_2, and more suitable reagents for trialling would be the palladium(0) complexes of dibenzylideneacetone (dba). These complexes are air stable and contain dba weakly bound to palladium, and hence they are easily displaced. Several different complexes are known, but the most useful are those of formulation $\{Pd_2(dba)_3 \cdot S\}$ (S=$CHCl_3$, C_6H_6 and $C_6H_5(CH_3)$).[20] In this case the complex $\{Pd_2(dba)_3 \cdot CHCl_3\}$ was employed as it can be prepared in 80% yield.[20]

Preliminary studies were confined to the attempted preparation of the stable complex {PdMeI(bipy)}. It was found that reaction of $\{Pd_2(dba)_3 \cdot CHCl_3\}$ with 2.4 mole equivalents of MeI in benzene, followed by 2 mole equivalents of bipy, gave, after 12 hours stirring, ~4% of the desired complex and a brown residue (unidentified) equation 3.3.1-7a. A similar reaction, with a large excess of MeI and with heating to 55°C gave, after 30 minutes, 79% of the desired complex {PdMeI(bipy)}, equation 3.3.1-7b.



4 % {PdMeI(bipy)} 3.3.1-7a

79% {PdMeI(bipy)} 3.3.1-7b

Extension of this approach using other bidentate and tridentate ligands, met with limited success. The employment of weak donor ligands, *e.g.* pz_2CH_2, gave low yields (~10%), with purification difficult due to the low stability of the complexes; but the use of strong donor ligands, *e.g.* py_2CH_2, gave higher yields (~40%).

As a **general** synthetic route to monoorganohalopalladium(II) complexes the procedure appeared not to be viable and was not studied further.

(ii) Oxidative Addition to Pd(II)

All reported examples of monoalkylhalopalladium(II) complexes containing bidentate N-donor ligands have been prepared by the reaction of an organohalide with a diorganopalladium(II) complex, except perhaps for {PdMeCl(bipy)},[30] for which a preparative method was not given.[30]

The preparation of monomethyliodopalladium(II) complexes was investigated *via* a similar reaction. Reaction of the complexes $\{PdMe_2(L_2)\}$ (L_2=bidentate N-donor ligands) with MeI in either acetone or benzene at ambient temperature occurred rapidly and cleanly to yield the complexes $\{PdMeI(L_2)\}$ in high yield; frequently the evolution of a gas was observed, and was assumed to be ethane, equation 3.3.1-8. The reaction was also extremely facile at 0°C (and indeed below 0°C), and hence readily allowed isolation of more unstable complexes, *e.g.* $\{PdMeI(pz_2CH_2)\}$.

$$\{PdMe_2(L_2)\} + MeI \rightarrow \{PdMeI(L_2)\} + MeMe \qquad 3.3.1\text{-}8$$

The proposed mechanism for this reaction is *via* oxidative addition of MeI to $\{PdMe_2(L_2)\}$ to give a transient Pd(IV) intermediate, *i.e.* '$Pd^{IV}Me_3I(L_2)$', which

reductively eliminates ethane to form {PdMeI(L_2)}. Evidence for this mechanism was obtained by monitoring the reaction of {$PdMe_2$(bipy)} with MeI using ^{1}H N.M.R. spectroscopy (see chapter 5). Reaction of {$PdMe_2$(bipy)} with MeI at ambient temperature gave a spectrum assignable as {$PdMe_3I$(bipy)}, *i.e.* one bipy environment and two Pd-Me environments in 2:1 ratio. The spectra changed over 30 minutes to give a final spectrum assignable as a mixture of {PdMeI(bipy)} and ethane (confirmed from a ^{1}H N.M.R. spectrum of an authentic sample); purging of this solution with N_2 gas gave {PdMeI(bipy)} as the only remaining species in solution. Similar mechanisms have been proposed previously for related reactions,[22] but the Pd(IV) intermediate(s) could not be detected.

$$\{PdMe_2(L_2)\} + MeI \rightarrow \text{'}PdMe_3I(L_2)\text{'} \rightarrow \{PdMeI(L_2)\} + MeMe \qquad 3.3.1\text{-}9$$

The major disadvantage of this process for synthesis is that prior preparation of the corresponding dimethylpalladium(II) complex is necessary. Such complexes are frequently unstable, *e.g.* {$PdMe_2(pz_2CHMe)$}, or cannot be readily prepared, *e.g.* complexes containing groups sensitive to alkyl lithium reagents.

(c) Bridge-Splitting Reactions with {$PdMe(\mu\text{-}X)(SMe_2)\}_2$

A route which was found to have general applicability is the reaction of the iodo-bridged dimer {$PdMe(\mu\text{-}I)(SMe_2)\}_2$ with ligands (L_2). This method involved reaction of {$PdMe(\mu\text{-}I)(SMe_2)\}_2$ with 2 mole equivalents of L_2 in either acetone or benzene at ambient temperature; work-up afforded the desired complex {PdMeI(L_2)} in moderate to high yield, equation 3.3.1-10.

$$\{PdMe(\mu\text{-}I)(SMe_2)\}_2 + 2\,L_2 \rightarrow 2\,\{PdMeI(L_2)\} \qquad 3.3.1\text{-}10$$

L_2=nitrogen donor ligands

This procedure has been used to prepare monomethyliodopalladium(II) complexes with a wide variety of ligands, containing a range of functional groups, for example, pymimCH_2 pymim$C{=}CH_2$, pymim$C{=}O$. However, with py_2CO an intractable solid, which could not be recrystallised or studied by ^1H N.M.R. spectroscopy, was obtained. The near infrared spectrum of this solid exhibited strong υ(OH) absorptions (and other ligand absorptions), but no absorption corresponding to υ(C=O). Also, melting point behaviour of the solid was characteristic of complexes which contain a Pd-Me bond†. Based on this information the formulation $\{PdMeI(py_2C(OH)_2)\}$ is proposed. The hydration of py_2CO to form geminal diols upon complexation with metal ions has been reported previously.[45]

A similar series of reactions also occurs readily between the chloro- and bromo-analogues $\{PdMe(\mu\text{-}X)(SMe_2)\}_2$ (X=Cl, Br) and L_2, to yield the complexes $\{PdMeX(L_2)\}$. An alternative method involving replacement of the iodo-group in $\{PdMe(\mu\text{-}I)(SMe_2)\}_2$ with the desired halogen (X), followed by reaction with L_2 to give the complexes $\{PdMeX(L_2)\}$ is more convenient as it allows preparation of methylchloro- and methylbromopalladium(II) complexes from a single palladium(II) substrate, in yields greater than that obtained by direct reaction of the respective halogeno-bridged dimer.

The sequence involved removal of the iodo-group in $\{PdMe(\mu\text{-}I)(SMe_2)\}_2$ with $AgNO_3$, followed by addition of halide ion (KX), and ligand (L_2) to afford the complexes $\{PdMeX(L_2)\}$, scheme 3.3.1-3.

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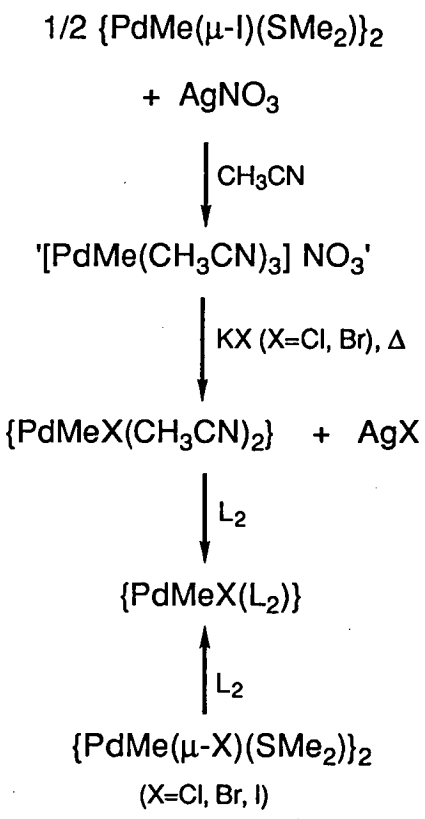
† all complexes which contain at least one PdMe bond decompose violently prior to melting, with the evolution of a gas (unidentified).

Scheme 3.3.1-3.



3.3.2 Characterisation of the Complexes {PdMeX(L_2)}

The monomethylhalopalladium(II) complexes prepared above were characterised by microanalysis (CHN), and ^{1}H N.M.R. and mass spectroscopy. Microanalysis and ^{1}H N.M.R. spectra (see chapter 4 for assignments) were consistent with the formulation {PdMeI(L_2)}, *i.e.* ^{1}H N.M.R. spectra show a 1:1 ratio of Pd**Me** and Pd($\mathbf{L_2}$) resonances. Mass spectra of the complexes were similar to that exhibited by the halo-bridged dimers {PdMe(μ-x)(SMe_2)}$_2$, *i.e.* with production of the fragments MeX, HX, X and L_2.

All of the complexes are yellow-orange, and are notably more stable than their dimethylpalladium(II) analogues; an increase in melting point of 30-40°C was common on passing from {$PdMe_2(L_2)$} to analogous complexes {PdMeX(L_2)}. Recrystallisation of the complexes was readily achieved using an acetone/hexane

solvent mixture. The use of halogenated solvents, *e.g.* $CHCl_3$ and CH_2Cl_2, for recrystallisations was in general avoided due to the detrimental effect these solvents may have on methylpalladium(II) complexes.

Complexes prepared by the methods described in the preceding pages, including yields obtained, are listed in Table 3.3.2-1.

Table 3.3.2-1. Preparation of $\{PdMeX(L_n)\}$ Complexes and Yields Obtained

Ligand	Method of Preparation, Yield	Ligand	Method of Preparation Yield
pz_2CH_2	a, 51%	$pypzCH_2$	b, 57%
pz_2CHMe	a, 69%	$mimpzCH_2$	b, 58%
pz_2CMe_2	a, 73%	$pypz_2CH$	b, 62%
pz_3CH	a, 46%	$mimpz_2CH$	b, 72%
$MeSCH_2CH_2SMe$	a, 69%	$mimpy_2CH$	b, 46%
pz_4C	b, 49%	$pymim_2CH$	b, 46%
py_2CH_2	b, 76%	bipy	b, 79%
py_2CHMe	b, 71%	phen	b, 78%
py_2CMe	b, 62%	pymim	b, 81%
$py_2C{=}CH_2$	b, 71%	PPh_3	b, 82%
py_3CH	b, 62%	mim_2CH_2	b, 89%
mim_2CO	b, 88%	mim_2CHMe	b, 73%
$mim_2C{=}CH_2$	b, 82%	$pymimCH_2$	b, 76%
pymimCHMe	b, 76%	$pymimC{=}CH_2$	b, 66%
pymimCO	b, 68%		

(a) $\{PdCl_2(SMe_2)\} + MeLi/LiI + L_n \rightarrow \{PdMeI(L_n)\}$

(b) $\{PdMe(\mu\text{-}I)(SMe_2)\}_2 + 2\,L_n \rightarrow \{PdMeI(L_n)\}$

3.4 PREPARATION of MONOMETHYLPALLADIUM(II) CATIONS

The iodo-bridged dimer $\{PdMe(\mu\text{-}I)(SMe_2)\}_2$ was also employed in this study for the preparation of cationic monomethylpalladium(II) complexes. This was achieved by either direct reaction of the ligands with $\{PdMe(\mu\text{-}I)(SMe_2)\}_2$, or by prior removal of the iodo-group. The complexes were characterised by microanalysis, ^1H N.M.R. spectroscopy, and, for $[PdMe(\gamma\text{-pic})(bipy)]BF_4$, crystals suitable for a crystallographic study were obtained and the structure subsequently determined by Dr. A. H. White.and colleagues of the University of Western Australia.

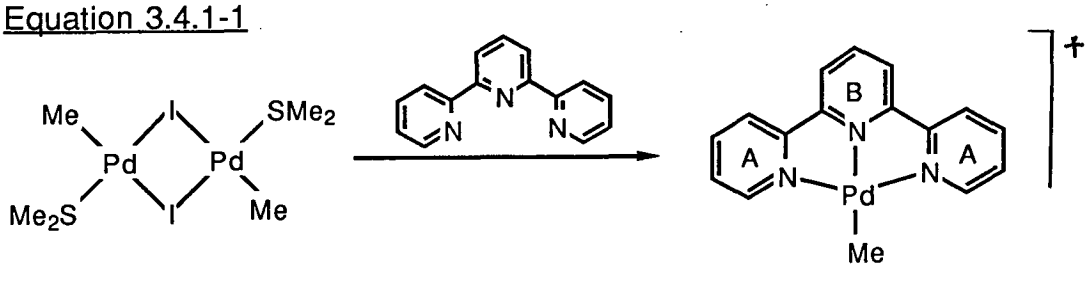
3.4.1 Preparation and Characterisation of the Complexes

(i) Directly from $\{PdMe(\mu\text{-}I)(SMe_2)\}_2$

Reaction of the iodo-bridged dimer with two mole equivalents of terpy immediately gave a pale yellow precipitate in high yield (87%). The solid formed was only sparingly soluble in common organic solvents and could not be readily recrystallised, although a microanalysis (CHN), and a ^1H N.M.R. spectrum of the complex in DMSO-D6/CD_3OD are consistent with the formulation [Pd(terpy)Me]I.

The N.M.R. spectrum revealed a ligand:PdMe ratio of 11H : 3H or 1Ligand : 1PdMe, and the aromatic region displayed the presence of two pyridine ring environments in 2:1 ratio, *i.e.* rings A and B for the proposed structure in equation 3.4.1-1. It should also be noted that the spectra displayed other spurious resonances (singlets) which have been assigned, due to the low solubility of [PdMe(terpy)]I, as minor impurities in the complex or deuterated solvent (DMSO-D6/CD_3OD).

Equation 3.4.1-1



While terpy was the only ligand examined for the direct preparation of cationic complexes, potentially other planar tridentate ligands may react to give complexes of the form $[PdMe(L_3)]I$ (L_3=planar tridentate ligand). It is interesting to note that the analogous $Pt^{II}Me$ complex does not appear to have been reported.

(ii) By prior removal of I^- in $\{PdMe(\mu\text{-}I)(SMe_2)\}_2$.

In section 3.3.1c, preparation of the complexes $\{PdMeX(L_2)\}$ (X=Cl, Br; L_2=chelating N-donor ligands) from $\{PdMe(\mu\text{-}I)(SMe_2)\}_2$, *via* halide exchange reactions, was discussed. A similar procedure, but with addition of a donor solvent (S) in place of the halide ion (X^-), was used to prepare the cationic complexes $[PdMe(S)(L_2)]^+$.

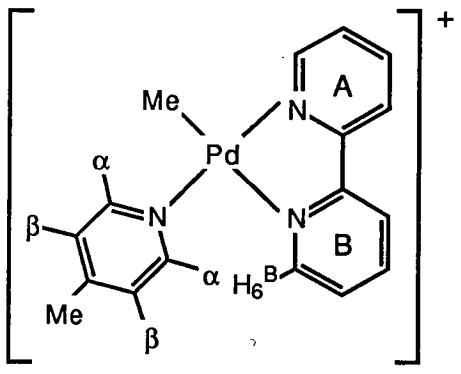
The procedure involved removal of the iodo-group from $\{PdMe(\mu\text{-}I)(SMe_2)\}_2$ with $AgBF_4$, in the presence of a donor solvent (S), filtration to remove precipitated AgI, followed by addition of the ligand (L_2) to give the complexes $[PdMe(S)(L_2)]BF_4$, equation 3.4.1-2. This preparative route was investigated for L_2=bipy, and S=γ-picoline (γ-pic) and CH_3CN.

$$\{PdMe(\mu\text{-}I)(SMe_2)\}_2 \xrightarrow[S]{AgBF_4} \xrightarrow{L_2} '[PdMe(S)(SMe_2)]BF_4' \qquad 3.4.1\text{-}2$$

(a) $[PdMe(\gamma\text{-pic})(bipy)]BF_4$

The reaction for S=γ-pic and L_2=bipy gave a white crystalline solid in moderate yield (65%). The solid could be recrystallised readily from acetone/hexane, and a microanalysis (CHN), consistent with the formulation $[PdMe(\gamma\text{-pic})(bipy)]BF_4$ was obtained. The ^1H N.M.R. spectrum of the complex in $(CD_3)_2CO$ revealed a 1:1:1 ratio of methyl, γ-picoline, and bipy ligands, with bipy resonances arising from two inequivalent pyridine rings (rings A and B in figure 3.4.1-1) and thus the complex is readily assigned the structure shown.

Figure 3.4.1-1.



The aromatic region of the ^1H N.M.R. spectrum is shown in figure 3.4.1-2 and has been fully assigned with the aid of the COSY spectrum, figure 3.4.1-3. Assignment of resonances arising from the aromatic γ–picoline protons, H_α^D and H_β^D, follows directly from their integration values (2H each), multiplicities (doublets), and observed connectivity in the COSY spectrum. Similarly, assignment of the pyridine resonances, H_6, H_5, H_4 and H_3, within each ring system (A and B) is possible from their observed multiplicities (see chapter 4 for discussion) and observed connectivity in the COSY spectrum.

Further, assignment of ring B as *cis* to γ–picoline is possible by noting the upfield shift (*ca.* 1 ppm) of H_6^B compared with the H_6 proton of ring A (*cis* to methyl). This shielding is a result of the spatial proximity of H_6^B to the coordinated γ–picoline ligand, which is constrained, due to steric interactions between H_α^D and H_6^B, to lie nearly perpendicular to the plane of the metal (see section 3.4.2).

^1H N.M.R. spectra of $[PdMe(\gamma\text{–pic})(bipy)]BF_4$ in CD_3CN were similar to those obtained for the complex in $(CD_3)_2$ CO (described above); spectra obtained in pyridine-D5 (py-D5), however, were substantially different. While spectra of the complex in py-D5 displayed a 1:1:1 ratio of methyl, γ–picoline, and bipy environments, as indeed found in $(CD_3)_2CO$ and CD_3CN, the pyridine rings of bipy, in this instance, were equivalent, figure 3.4.1-4.

Figure 3.4.1-2. ^{1}H NMR of [PdMe(γ-pic)(bipy)]BF_4 in Acetone-D6

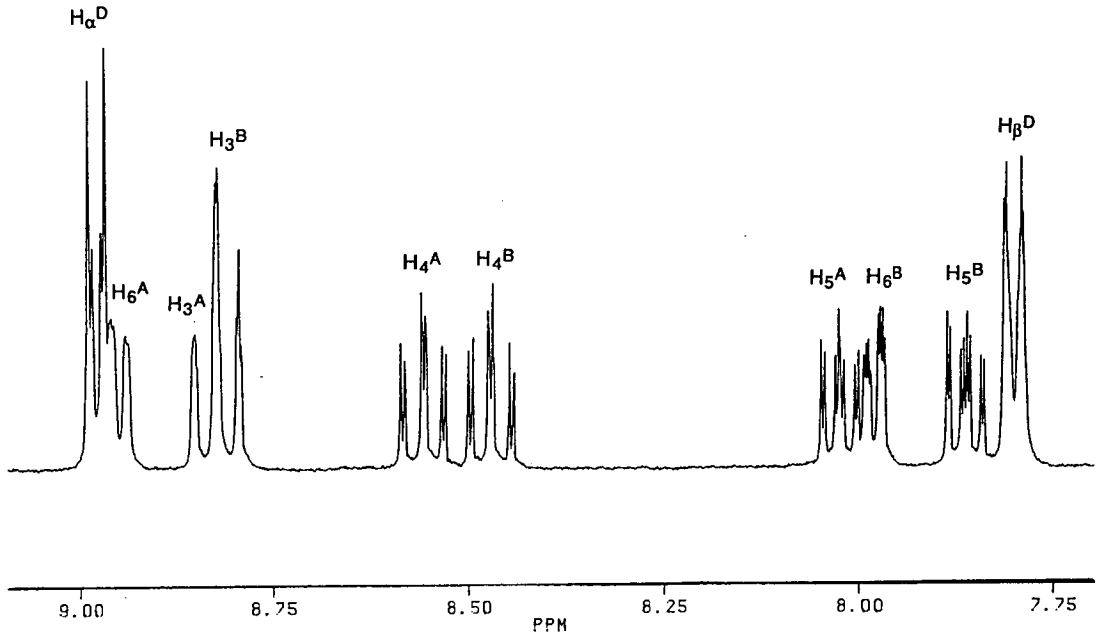


Figure 3.4.1-3. COSY Spectrum of [PdMe(γ-pic)(bipy)]BF_4 in Acetone-D6

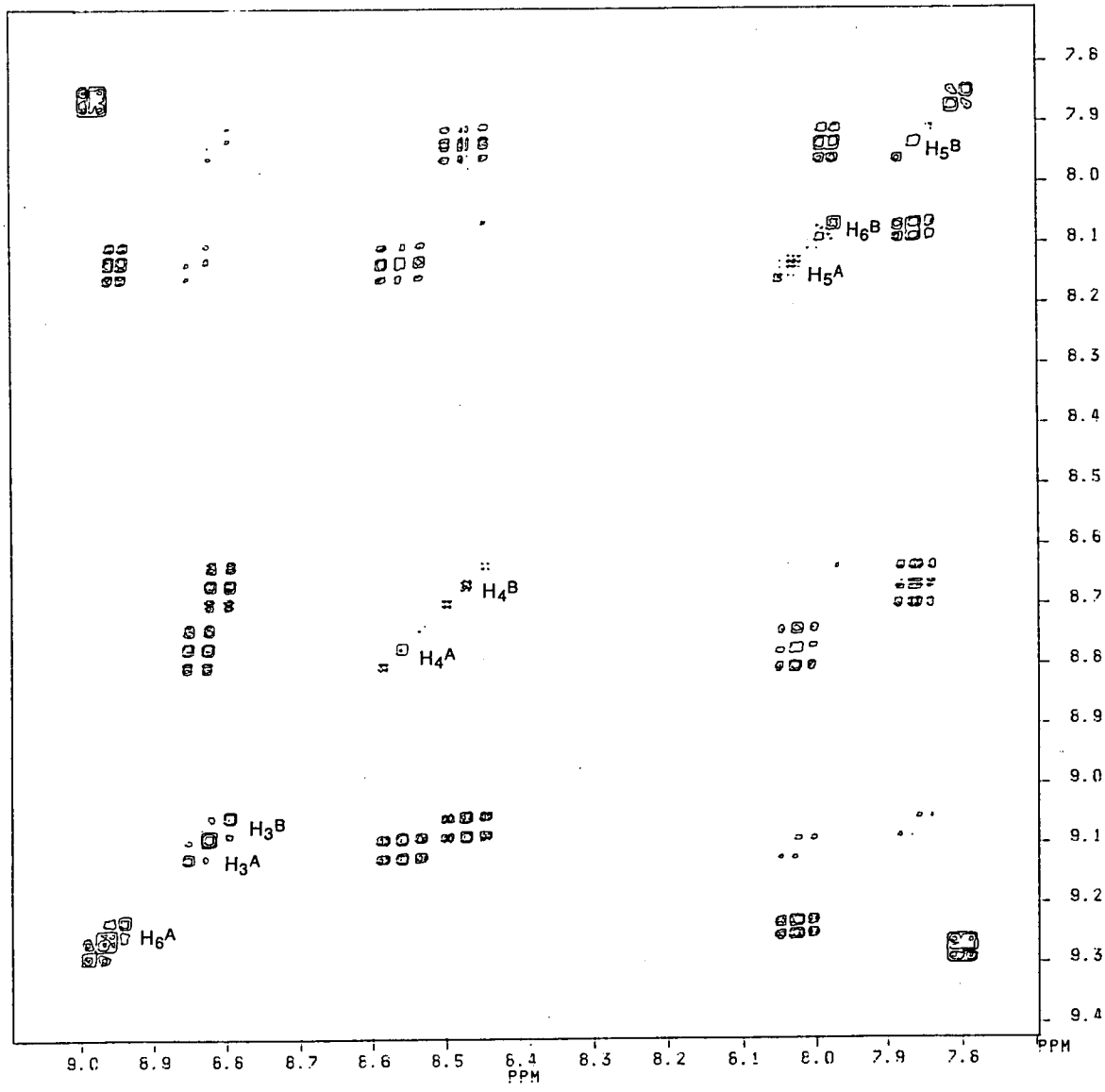
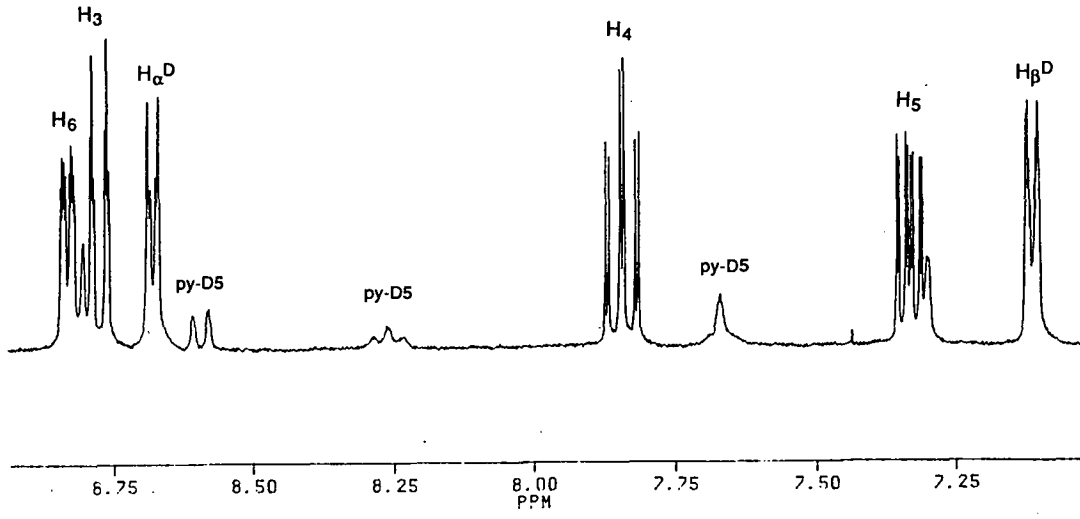
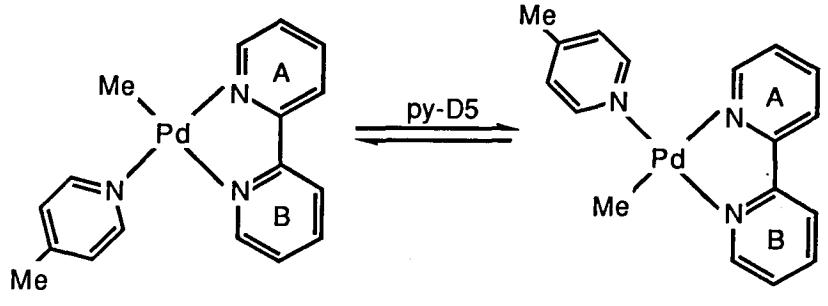


Figure 3.4.1-4. ^1H NMR of $[PdMe(\gamma\text{-pic})(bipy)]BF_4$ in pyridine-d5



The equivalence of both halves of the bipy ligand is assumed to result from solvent induced rapid site exchange of the methyl and γ-picoline ligands, equation 3.4.1-3. The mechanism for this reaction is thought to involve formation of a transient five coordinate intermediate of sufficient lifetime to allow internal rearrangement of Me and γ-pic ligands.[46] Further, as py-D5 and γ-picoline are expected to exhibit similar donor abilities, either may be eliminated from the five coordinate intermediate, with the formation of $[PdMe(py\text{-}D5)(bipy)]BF_4$ kinetically favoured due to the large quantity of py-D5 present. Evidence for the displacement of γ-picoline is provided by the observation that free γ-picoline in py-D5 exhibits an identical spectrum to γ-picoline in $[PdMe(\gamma\text{-pic})(bipy)]BF_4$ (in py-D5).

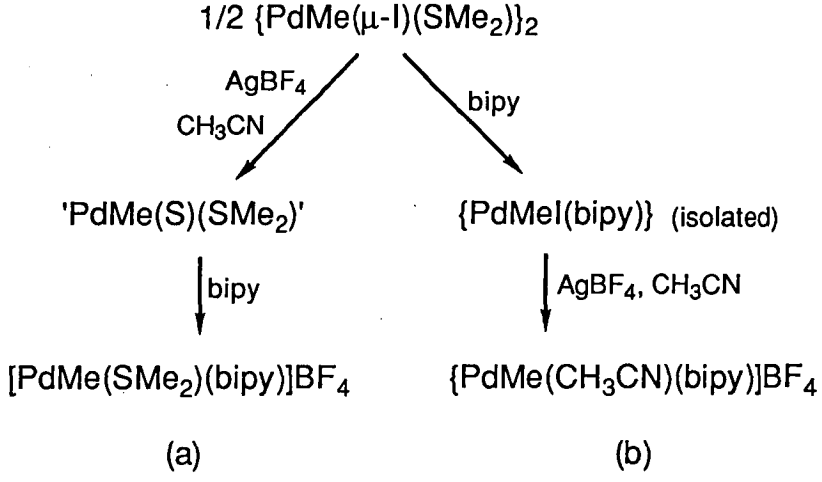


3.4.1-3

(b) [PdMe(CH_3CN)(bipy)]BF_4

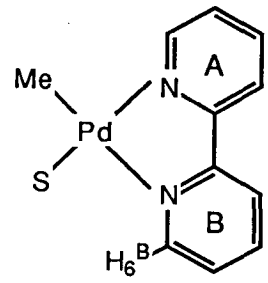
The reaction of {PdMe(μ-I)(SMe_2)}$_2$ with S=CH_3CN and L_2=bipy, according to equation 3.4.1-2, gave the unexpected product [PdMe(SMe_2)(bipy)]BF_4 in moderate yield (63%) as a white semi-crystalline solid, scheme 3.4.1-1 (route a). This presumably occurs as a result of the preference of Pd(II) for the ligand SMe_2, rather than CH_3CN. The complex [PdMe(CH_3CN)(bipy)]BF_4 may be readily prepared, however, by the reaction of {PdMeI(bipy)} with $AgBF_4$ in the presence of CH_3CN, scheme 3.4.1-1 (route b). This reaction sequence afforded [PdMe(CH_3CN)(bipy)]BF_4 in high yield (76%), as a white powder.

Scheme 3.4.1-1.



For the ^1H N.M.R. spectrum of [PdMe(SMe_2)(bipy)]BF_4 in $CDCl_3$, full assignment of the aromatic region (with the aid of a COSY spectrum) has been possible, including assignment of ring A as *cis* to methyl and ring B as *cis* to SMe_2, figure 3.4.1-5a and figure 3.4.1-6a. This assignment followed from the observation that H_6^B is approximately 0.2 ppm downfield from H_6^A, consistent with deshielding of H_6^B as a result of the close proximity (of H_6^B) to the electron rich S atom.

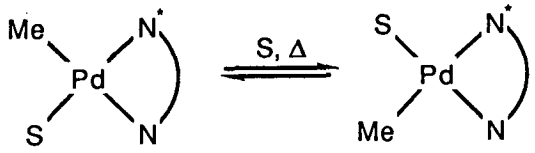
Figure 3.4.1-6



(a) $S=SMe_2$ (b) $S=CH_3CN$

Using similar approaches, the spectrum of $[PdMe(CH_3CN)(bipy)]BF_4$ in CD_3CN has also been assigned, although in this case the downfield shift of H_6^B is not as pronounced, figure 3.4.1-5d, and the assignment of ring A and B in figure 3.4.1-6b is tentative.

The ^1H N.M.R. spectra of $[PdMe(S)(bipy)]BF_4$ ($S=SMe_2$, CH_3CN) in CD_3CN or $(CD_3)_2CO$, at ambient temperature exhibit broad resonances in the aromatic region, compared with the spectra in $CDCl_3$, and has been attributed to slow exchange of pyridine ring environments in the bipy ligand. Consistent with this interpretation, the resonances 'sharpened' on warming the solution to give a single ring environment, while cooling the solution gave more clearly discernible environments, for example $[PdMe(SMe_2)(bipy)]BF_4$ in $(CD_3)_2CO$, figure 3.4.1-7. Such behaviour is consistent with temperature dependent, solvent induced site exchange of Me and SMe_2 groups, equation 3.4.1-4, and a similar mechanism to that described for $[PdMe(\gamma\text{-pic})(bipy)]BF_4$ applies.



3.4.1-4

Figure 3.4.1-5. ^{1}H NMR of [PdMe(S)(bipy)]BF_4 in $CDCl_3$, CD_3CN, or $(CD_3)_2CO$

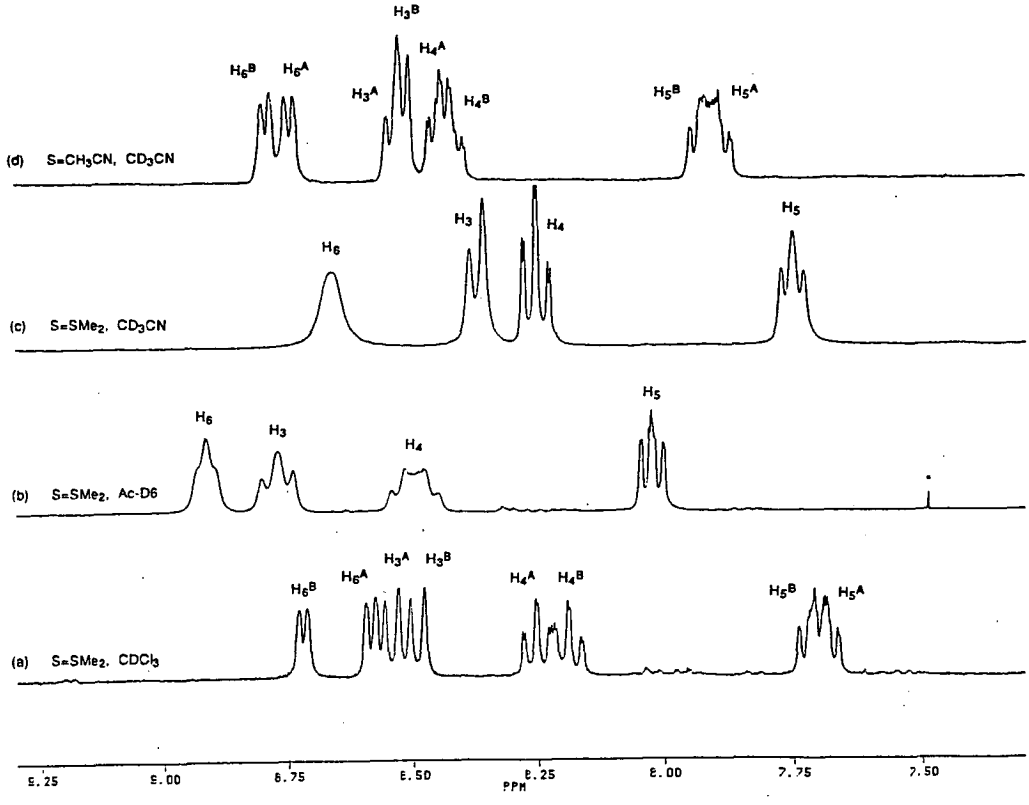
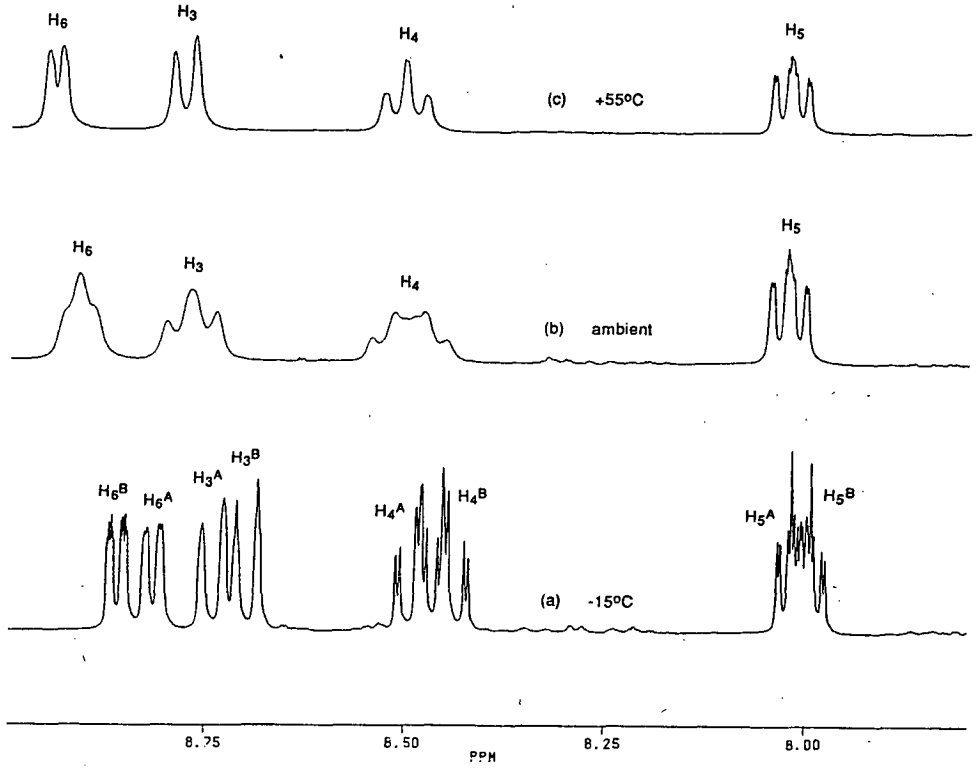


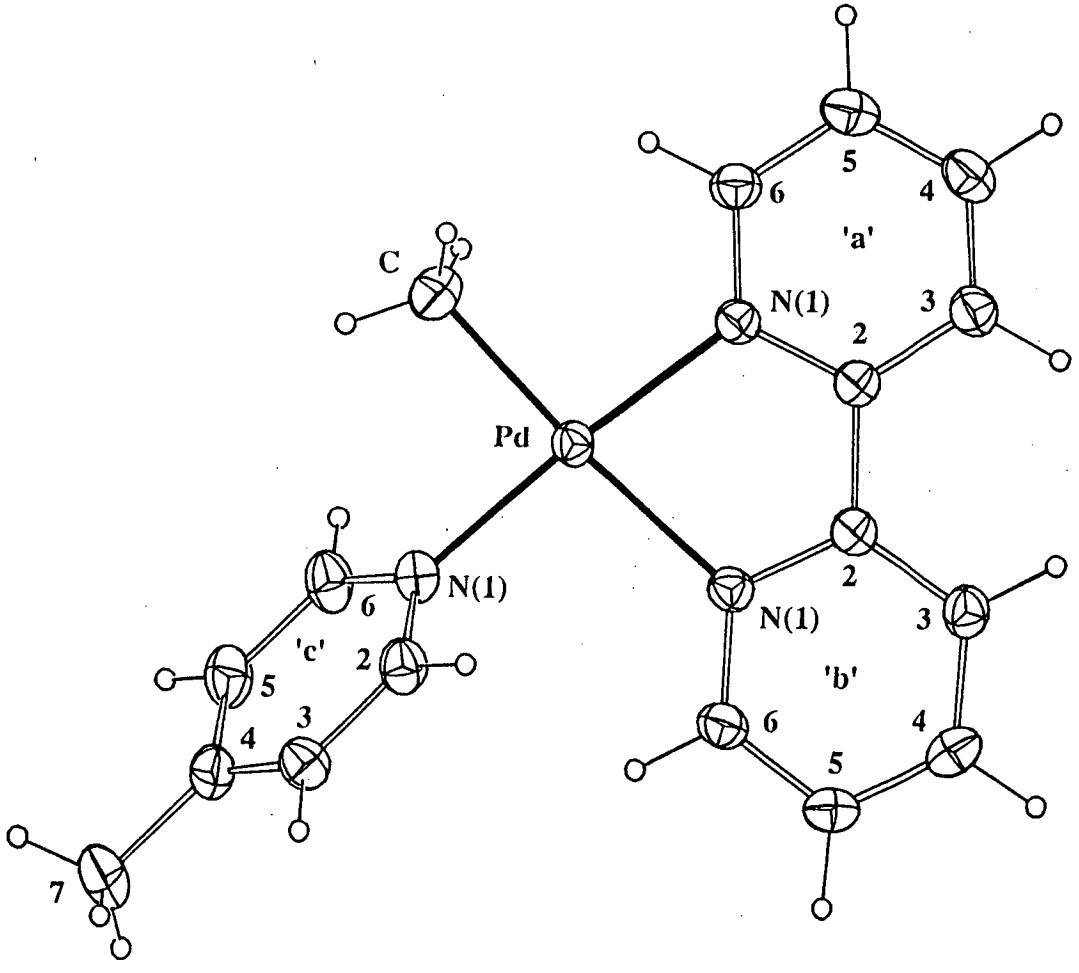
Figure 3.4.1-7. Variable Temperature ^{1}H NMR Spectra of [PdMe(SMe_2)(bipy)] in Acetone-D6



3.4.2 Solid State Structure of [PdMe(γ–pic)(bipy)]BF_4

Crystals of the complex [PdMe(γ–pic)(bipy)]BF_4 suitable for a structural study were obtained by dissolution of the complex in acetone (facilitated by the addition of a small quantity of dichloromethane), followed by exposure to diethyl ether vapour in a sealed chamber at ambient temperature. The [PdMe(γ–pic)(bipy)]$^+$ cation is shown in figure 3.4.2-1, and selected bond lengths and angles are given in table 3.4.2-1.

Figure 3.4.2-1.



Palladium exhibits square planar geometry with the smallest bond angle being observed for bipy {N(a1)-Pd-N(b1)} 79.1(2)°. The C, N(a1), N(b1) and N(c1) atoms alternate above and below the mean plane 'PdCN$_3$', with a maximum deviation from this plane of -0.037Å (for C).

The three 'C_5N' rings (a,b,c) are planar and form dihedral angles, with the '$PdCN_3$' plane, of 2.1, 2.1° for bipy, and 62.1° for γ-picoline. The two planes of bipy form a dihedral angle of 1.5° with each other. The BF_4^- anion is not coordinated to palladium, as the shortest Pd....F contact is 3.981(5)Å.

The complex provides a good example of the *trans* effect of the methyl group, with Pd-N(b1) (2.131(4)Å) *trans* to Me longer than Pd-N(a1, c1) (2.049(4) and 2.033(4)Å respectively) *cis* to Me. Similar results have been reported for the *trans* N-O isomer of bis(glycinato)-*cis*-dimethylplatinum(IV),[47] where it was found that bonds *trans* to Me were elongated compared with bonds *cis* to Me.

Table 3.4.2-1. Coordination Geometry for the Palladium Atom in [MePd(bipy)(γ-pic)]BF_4; Distances in Å. Angles in °

Pd-C[a]	2.036(6)	Pd-N(b1)	2.131(4)
Pd-N(a1)	2.049(4)	Pd-N(c1)	2.033(4)
C-Pd-N(a1)	95.4(2)	Pd-N(a1)-C(a2)	116.0(3)
C-Pd-N(b1)	174.3(2)	Pd-N(a1)-C(a6)	125.8(3)
C-Pd-N(c1)	88.1(2)	Pd-N(b1)-C(b2)	113.1(3)
N(a1)-Pd-N(b1)	79.1(2)	Pd-N(b1)-C(b6)	128.8(3)
N(a1)-Pd-N(c1)	176.4(2)	Pd-N(c1)-C(c2)	120.9(4)
N(b1)-Pd-N(c1)	97.4(2)	Pd-N(c1)-C(c6)	121.0(3)
Deviation (Å) of atoms from the 'CN3' plane[b]			
Pd	0.002	N(b1)	-0.016
C	-0.037	N(c1)	0.017
N(a1)	0.017		

[a] The shortest Pd F contact is Pd F(3), 3.981(5) Å.

[b] The mean plane has χ^2 51.6. The 'C5N' rings (a,b,c) have χ^2 1.2, 7.4, and 2.4, respectively; they form dihedral angles of 2.1, 2.1, and 62.1° with the 'C3N' plane, the Pd atom lies 0.061, 0.001 and 0.117 Å from the mean planes, and the two planes of bipy form a dihedral angle of 1.5°.

REFERENCES

1. Heck, R.F.,

   Pure Appl Chem., **50** (1978) 691.

2. For the proposed mechanism see, for example,

   Schoenberg, A., and Heck, R.F.,

   J. Am. Chem. Soc., **96** (1974) 7761.

3. Calvin, G., and Coates, G.E.,

   J. Chem. Soc., (1960) 2008.

4. Calvin, G., and Coates, G.E.,

   Chem. Indust., **78** (1958) 160.

5. Wozniak, B., Ruddick, J.D., and Wilkinson, G.,

   J. Chem. Soc. (A), (1971) 3116.

6. Sergi, S., Faraone, F., Silvestro, L., and Pietropaolo, R.,

   J. Organomet. Chem., **33** (1971) 403.

7. Maitlis, P.M.,

   "The Organic Chemistry of Palladium" Vol. 1, Pg 70.

   Academic Press, London, 1971.

8. Stakem, F.G., and Heck, R.F.,

   J. Org. Chem., **45** (1980) 3584.

   Crociani, B., Nicolini, M., and Richards, R.L.,

   J. Organomet. Chem., **104** (1976) 259.

9. Suggs, J.W., and Lee, K.S.,

J. Organomet. Chem., **299** (1986) 297.

Yamamoto, Y., and Yanagi, A.,

Chem. Pharm. Bull., **30** (1982) 2003.

10. Heck, R.F.,

J. Am. Chem. Soc., **90** (1968) 5518, 5526, 5531, 5535, 5538, 5542.

11. Maitlis, P.M.,

"The Organic Chemistry of Palladium", Vol 2.

Academic Press, London, 1971.

12. Negishi, E.,

"Organometallics in Organic Synthesis", Vol. 1.

John Wiley and Sons, Chichester, 1980.

13. Trost, B.M., and Verhoeven, T.R.,

"Organopalladium Compounds in Organic Synthesis and in

Catalysis"in "Comprehensive Organometallic Chemistry",

Wilkinson, G., Stone, F.G.A., and Abel, E.W. (Eds.),

Pergamon Press, Oxford, **8** (1982) 799.

14. Parshall, G.W.,

J. Am. Chem. Soc., **96** (1974) 2360.

Fitton, P., and Rick, E.A.,

J. Organomet. Chem., **28** (1971) 287.

15. Tanaka, H., Isobe, K., Kawaguchi, S., and Okeya, S.,

Bull. Chem. Soc. Jpn., 57 (1984) 456.

Isobe, K., Nakamura, Y., Miwa, T., Kawaguchi, S.,

Bull. Chem. Soc. Jpn., **60** (1987) 149.

16. Fitton, P., McKeon, J.E., and Ream, B.C.,

J. Chem. Soc. Chem. Commun., (1969) 370.

17. Kudo, K., Hidai, M., and Uchida, Y.,

J. Organomet. Chem., **33** (1971) 393.

Fitton, P., Johnson, M.P., and McKeon, J.E.,

J. Chem. Soc. Chem. Commun., (1968) 6.

18. Maitlis, P.M., Espinet, P., and Russell, M.J.H.,

"Complexes of Palladium(0)" in "Comprehensive Organometallic

Chemistry", Wilkinson, G., Stone, F.G.A., and Abel, E.W. (Eds.),

Pergamon Press, Oxford, 6 (1982) 243.

19. Clark, P.W., and Dyke, S.F.

J. Organomet. Chem., **281** (1985) 389.

20. Ukai, T., Kawazura, H., Ishii, Y., Bonnet, J.J. and Ibers, J.A.,

J. Organomet. Chem., **65** (1974) 253.

21. Ito, T.S., Hasegawa, S., Takahashi, Y., and Ishii, Y.,

J. Organomet. Chem., 73 (1974) 401.

22. See, for example,

(a) Gillie, A., and Stille, J.K.,

J. Am. Chem. Soc., **102** (1980) 4933.

(b) Diversi, P., Fasce, D., and Santini, R.,

J. Organomet. Chem., **269** (1984) 285.

(c) Cornioley-Deuschel, C., and von Zelewsky, A.,

Inorg. Chem., **26** (1987) 3354.

23.(a) Chatt, J., Vallarino, L.M., and Venanzi, L.M.,

J. Chem. Soc., (1957) 3413.

(b) Chatt, J., Vallarino, L.M., and Venanzi, L.M.,

J. Chem. Soc., (1957) 2496.

24. Holton, R.A., and Kjonaas, R.A.,

J. Am. Chem. Soc., **99** (1977) 4177.

25. Cope, A.C., and Siekman, R.W.,

J. Am. Chem. Soc., **87** (1965) 3272.

26. Parshall, G.W.,

Acc. Chem. Res., **3** (1970) 139.

27. See for example,

(a) Omae, I.,

Coord. Chem. Rev., **42** (1982) 245.

Constable, E.C.,

Polyhedron, **3** (1984) 1037.

Newkome, G.R., Puckett, W.E., Gupta, V.K. and Kiefer, G.E.,

Chem. Rev., **86** (1986) 451.

(b) Ryabov, A.D.,

Synthesis, (1985) 233.

28. Collman, J.P., Hegedus, L.S., Norton, J.R., and Finke, R.G., "Principles and Applications of Organotransition Metal Chemistry", University Science Books, California, 1987.

Tsuji, J., "Organic Synthesis by Means of Transition Metal Complexes" Springer-Verlag, Heidelberg, 1975.

29.(a) Bruce, M.I., *Angew. Chem. Int. Engl. Ed.*, **16** (1977) 73.

(b) Crociani, B., Boschi, T., Pietropaolo, R., and Belluco, U., *J. Chem. Soc.* (A), (1970) 531.

(c) Adams, H., Bailey, N.A., Briggs, T.N., McCleverty, J.A., and Colquhoun, H.M., *J. Chem. Soc. Dalton Trans.*, (1982) 1521.

(d) Hayashi, Y., Isobe, K., Nakamura, Y., and Okeya, S., *J. Organomet. Chem.*, **310** (1986) 127.

See also, for example,

Anderson, G.K., *Organometallics*, **2**, (1983) 665.

Vicente, J., Arcas, A., Borrachero, M.V. and Hursthouse, M.B., *J. Chem. Soc. Dalton Trans.*, (1987) 1655.

30. Chaudhury, N., Kekre, M.G., and Puddephatt, R.J., *J. Organomet. Chem.*, **73** (1974) C17.

31. Maitlis, P.M., and Stone, F.G.A.,

Chem. Indust., (1962) 1865.

32. De Renzi, A., Morelli, G., Panunzi, A., and Vitagliano, A.,

Gazz. Chim. Ital., 117 (1987) 445.

33. Goggin, P.L., Goodfellow, R.J., Haddock, S.R., Reed, F.J.S., Smith, J.G., and Thomas, K.M.,

J. Chem. Soc. Dalton Trans., (1972) 1904.

34. Langford, C.H., and Gray, H.B.,

"Ligand Substitution Processes", W.A. Benjamin, Inc., New York, 1965.

35. Stille, J.K.

"Oxidative Addition and Reduction Elimination" in

"The Chemistry of the Metal-Carbon bond", Vol. 2.

Hartley, F.R., and Patai, S. (Eds.), John Wiley and Sons Ltd., 1985.

36. See, for example,

(a) Visser, J.P., Jager, W.W., and Masters, C.,

Recl. Trav. Chim. Pays-Bas., 94 (1975) 70.

Tamaki, A., and Kochi, J.K.,

J. Organomet. Chem., 64 (1974) 411.

Rice, G.W., and Tobias, R.S.,

J. Organomet. Chem., 86 (1975) C37.

Puddephatt, R.J., and Thompson, P.J.,

J. Chem. Soc. Dalton Trans., (1975) 1810; (1977) 1219.

(b) Scott, J.D., and Puddephatt, R.J.,

Organometallics, **2** (1983) 1643.

(c) Uson, R., Fornies, J., Navarro, R., and Garcia, M.P.,

Inorg. Chim. Acta., **33** (1979) 69.

37. Lashanizadehgan, M., Rashidi, M., Hux, J.C., Puddephatt, R.J., and Ling, S.S.M.,

J. Organomet. Chem., **269** (1984) 317.

38. Windholz, M. (Ed.),

Merck Index, **10** (1983) 5908.

39. Goodfellow, R.J., Goggin, P.L., and Venanzi, L.M.,

J. Chem. Soc. (A), (1967) 1897.

40.(a) Goggin, P.L., Goodfellow, R.J., Sales, D.L., Stokes, J., and Woodward, P.,

J. Chem. Soc. (A), (1968) 31.

(b) Sales, D.L., Stokes, J., and Woodward, P.,

J. Chem. Soc. (A), (1968) 1852.

41. Goggin, P.L., Goodfellow, R.J., and Reed, F.J.S.,

J. Chem. Soc. Dalton Trans., (1974) 576.

42. Adams, D.M., and Chandler, P.J.,

J. Chem. Soc. Chem. Commun., (1966) 69.

43. Clark, R.J.H.,

Spectrochim. Acta, **21** (1965) 955.

44. Byers, P.K., Canty, A.J., Engelhardt, L.M., and White, A.H.,

J. Chem. Soc. Dalton Trans., (1986) 1731.

45. Byers, P.K., Canty, A.J., Engelhardt, L.M., Patrick, J.M.,

and White, A.H.,

J. Chem. Soc. Dalton Trans., (1985) 981.

46. See, for example,

Redfield, D.A., Nelson, J.H., Henry, R.A., Moore, D.W., and

Jonassen, H.B.,

J. Am. Chem. Soc., **96** (1974) 6298.

Anderson, G.K., and Cross, R.J.,

Chem. Soc. Rev., **9** (1980) 185.

47. Kennard, C.H.L., Hall, J.R., Eggins, R.G., Appleton, T.G., Agnew, N.H.,

and Smith, G.,

Cryst. Struct. Comm., **10** (1981) 1517.

CHAPTER 4

SOLUTION STATE BEHAVIOUR OF MONOMETHYL AND DIMETHYLPALLADIUM(II) COMPLEXES

4.1 INTRODUCTION

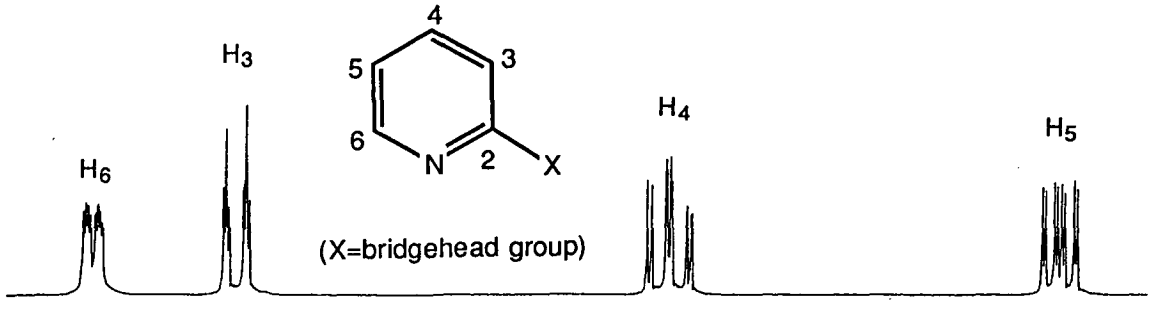
The solution state behaviour of all of the complexes prepared during this study has been extensively investigated using ^1H N.M.R. spectroscopy, and has resulted in the attainment of a wealth of data on conformational and variable temperature effects. To facilitate a logical and concise account of this behaviour, spectral interpretations for both the complexes $\{PdMe_2(L_2)\}$ and $\{PdMeX(L_2)\}$ are given together in this chapter.

Further, as all the bidentate and tridentate N-donor ligands used in this study are comprised of the heterocyclic groups pyridine, pyrazole and *N*-methylimidazole, it is instructive at this point to describe the assignment of protons for each of these rings:

(i) Pyridine Ring

The atom numbering scheme used is displayed in figure 4.1-1a, and a typical N.M.R. spectrum of a pyridine containing ligand, in this case py_2CH_2, is displayed in figure 4.1-1. All of the ligands used which contain a pyridine ring have pyridine functionalised at the 2-position, leaving protons H_6, H_5, H_4 and H_3. These protons are readily differentiated by their multiplicity and ^3J coupling constants, and assignment follows directly from the line shape.

Figure 4.1-1



The H_6 proton is readily assigned as it is nearly always the furthest proton downfield, and appears with the multiplicity d, dd, or ddd. However, despite the multiplicity observed, the $^3J_{5,6}$ coupling constant is *ca.* 5 Hz. The H_3 proton, on the

other hand, generally appears as a doublet, or less frequently a doublet with some fine structure present, but, in either case, the $^3J_{3,4}$ coupling constant is *ca.* 8 Hz.

The remaining protons, H_4 and H_5, are assigned from their line shape, with the H_4 proton appearing as a doublet of triplets (dt), or if resolution is poor, a triplet, and the H_5 proton appears as a ddd. Further, for ligands used in this study H_4 was generally downfield from H_5.

Some typical ^nJ coupling constants are given below:

H_6 : $^3J_{5,6}$ ~ 4.8, $^4J_{4,6}$ ~ 1.7, $^5J_{3,6}$ ~ 0.9 Hz

H_5 : $^3J_{4,5}$ ~ 7.6, $^3J_{5,6}$ ~ 4.8, $^4J_{3,5}$ ~ 1.2 Hz

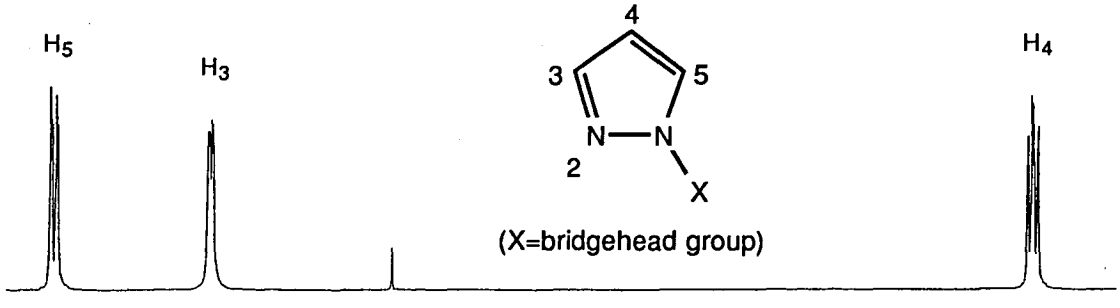
H_4 : $^3J_{3,4}$ ~ $^3J_{4,5}$ ~ 7.6, $^4J_{4,6}$ ~ 1.7 Hz

H_3 : $^3J_{3,4}$ ~ 8.0 Hz

(ii) Pyrazole Ring

For ligands which contain the pyrazole nucleus, functionalisation of pyrazole occurs at the (designated) 1-position, and gives the atom numbering scheme displayed in figure 4.1-2. Also, a typical N.M.R. spectrum of a pyrazole containing ligand, pz_2CH_2, is displayed in figure 4.1-2b. Criteria for the assignment of pyrazole protons have been given elsewhere,[1] but shall be summarised below.

Figure 4.1-2



As for pyridine protons, the H_3, H_4 and H_5 protons of pyrazole are assigned from their ^3J coupling constants and line shape. Thus, protons H_3 and H_5 are readily

discriminated from H_4, as the former frequently appear as doublets†, while the latter generally appears as a triplet†. Further, the H_4 protons are always upfield from the H_3 and H_5 protons.

The H_3 and H_5 protons are differentiated by noting that $^3J_{4,5}$ is always larger than $^3J_{3,4}$, the H_3 signal is less resolved than the H_5 signal, due to the nuclear quadrupole relaxation effect of N_2 on H_3, and the H_5 proton is more sensitive to solvent effects than the H_3 proton. An example of the last effect can be found by comparison of the ^1H N.M.R. spectra of pz_3CH in acetone and chloroform. In acetone the H_5 proton resonates at 7.86 ppm (relative to TMS) while in chloroform it appears at 7.58 ppm. The H_3 proton, on the other hand, resonates at 7.63 ppm in acetone, and remains virtually unchanged at 7.68 ppm in chloroform.

Coupling constants for the H_3, H_4 and H_5 protons of pz_3CH, which are representative of those typically found for pyrazole containing ligands, are given below:

H_3 : $^3J_{3,4}$ ~ 1.5 Hz

H_4 : $^3J_{4,(3,5)}$ ~ 2.1 Hz

H_5 : $^3J_{4,5}$ ~ 2.5 Hz

(iii) *N*-methylimidazole Ring

As for pyridine, *N*-methylimidazole is functionalised at the 2-position, and the resulting atom numbering scheme is shown in figure 4.1-3a. The ^1H N.M.R. spectrum of the *N*-methylimidazole moiety consists of a doublet for each of the H_4 and H_5 protons, and coupling constants of $^3J_{4,5}$ ~ 1Hz are commonly found. A typical N.M.R. spectrum is shown in figure 4.1-3b.

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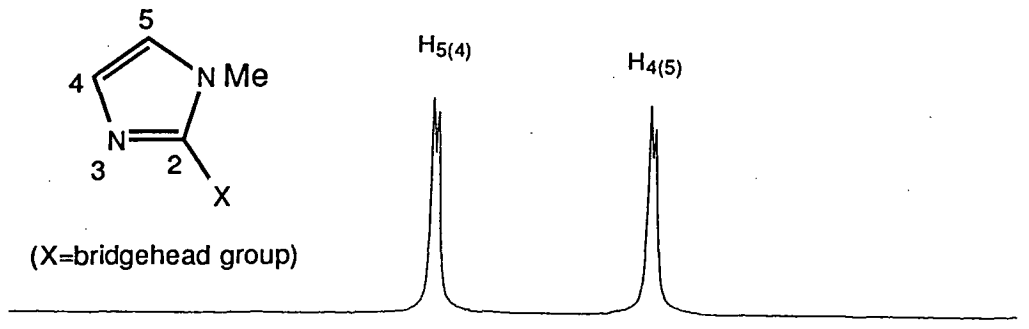
† H_3, H_4, and H_5 may also appear as a doublet of doublets (dd), although this occurs infrequently.

Figure 4.1-3.

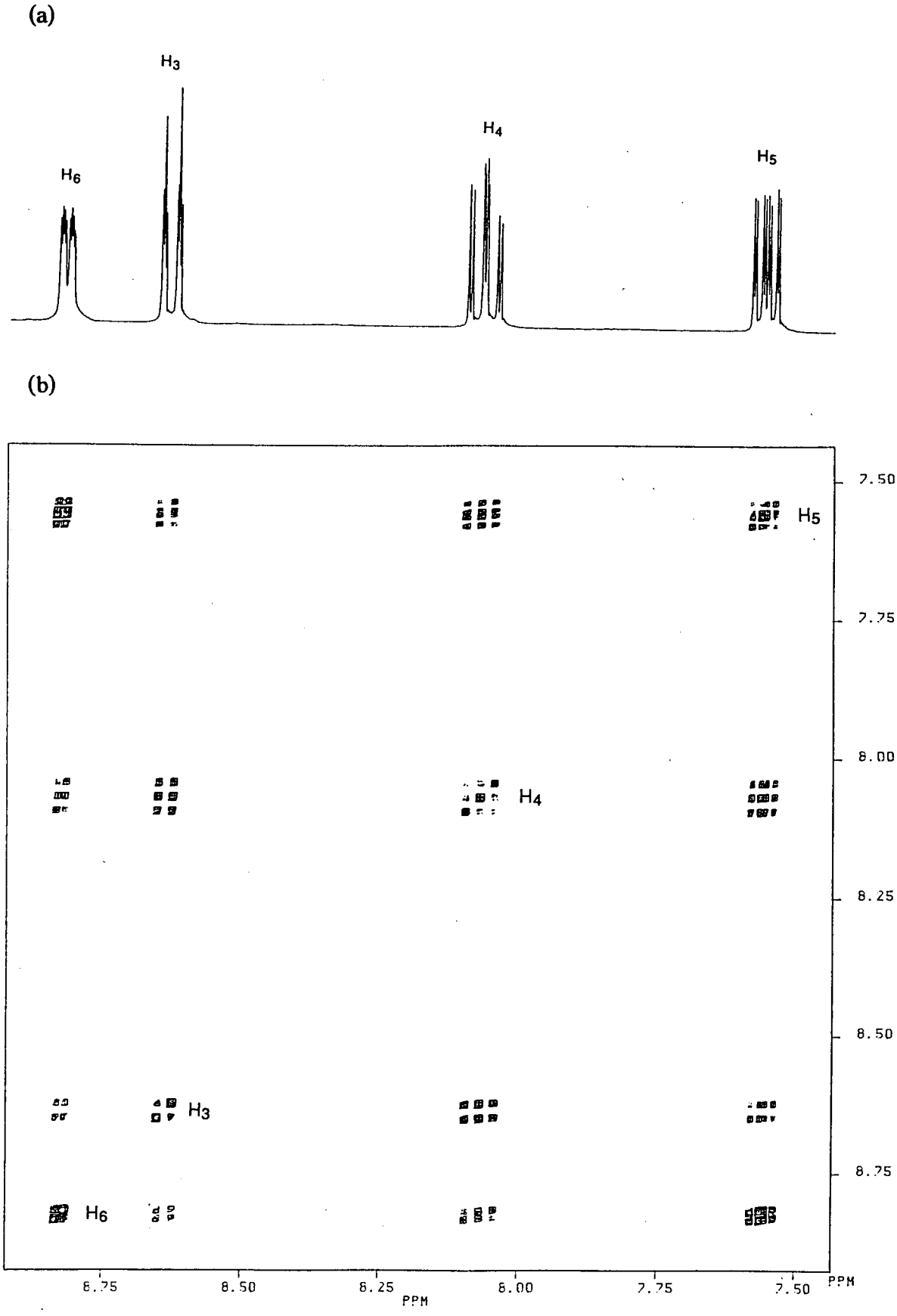


Criteria for differentiation of the H_4 and H_5 protons have been reported,[2] and differentiation is readily accomplished by obtaining spectra in two solvents. It was found that in non-polar solvents ($CDCl_3$) H_5 appears upfield from H_4, while in polar solvents (D_2O, Me_2SO-D6) the order is reversed.[2] An attempt to repeat this study for palladium complexes containing *N*-methylimidazole based ligands was not possible, owing to the unavailability of a range of complexes soluble in both deuterated acetone (polar solvent) and chloroform (non-polar solvent), and where assignment has not been possible these protons are referred to as $H_{4(5)}$ and $H_{5(4)}$.

A ^1H N.M.R. spectroscopic technique which has been used frequently during this study is shift correlated spectroscopy, or COSY, and is discussed here to illustrate the technique. Figure 4.1-4a displays the ^1H N.M.R. spectrum for the ligand bipy, and figure 4.1-4b displays its COSY spectrum.

The diagonal from lower left to upper right in the 2D spectrum represents the usual frequency versus intensity spectrum, with peak intensity represented by concentric contours. The contoured regions off the diagonal represent connectivity between coupled protons, and these regions are frequently referred to as **cross peaks.** For example, the coupling of H_6 (~8.8 ppm) to H_5 (~7.5 ppm) is indicated by lines drawn parallel to the frequency axis to the most intense cross peak, similarly for H_5 coupled to H_4, and H_4 coupled to H_3. As a general rule, the closer the coupled protons are to each other, *e.g.* ^3J versus ^4J coupling, the more intense the cross peak appears. This is illustrated by examination of the cross peaks adjacent to the H_6

Figure 4.1-4. ^{1}H NMR and COSY Spectra of 2,2'-bipyridyl



diagonal resonance. Thus, the cross peak representing $^3J_{5,6}$ coupling is more intense than that for $^5J_{3,6}$ coupling. Resonances which are not coupled, or are separated by large distances, show no cross peaks.

Finally, due to the adverse effects chlorinated solvents, *e.g.* $CHCl_3$ or CH_2Cl_2 usually have on complexes containing a $PdMe_2$ group, the majority of ^1H N.M.R. spectra were determined in deuterated acetone, or, for complexes of low solubility, dimethylsulphoxide. Acetone-D6 also proved to be the solvent of choice for variable temperature studies, due to its lower freezing point (-94°C) compared with acetonitrile (-44°C) or chloroform (-64°C).

4.2 METHYLPALLADIUM(II) COMPLEXES CONTAINING BIDENTATE LIGANDS

4.2.1 Dimethylpalladium(II) Complexes

^1H N.M.R. spectra of the complexes $\{PdMe_2(L_2)\}$ (L_2=bidentate N-donor ligands) were recorded in acetone-D6, or, in the case of $\{PdMe_2(mim_2CH_2)\}$, in dimethylsulphoxide-D6. Assignments follow directly from the observed multiplicity and integration value, with aromatic protons readily assigned from the discussion above. Further, all spectra recorded in deuterated acetone contain a quintet arising from incomplete deuteration of acetone, with the central peak occurring at 2.20 ppm, and a broad singlet at *ca.* 3 ppm due to H_2O/HDO. A spectrum typical of that normally observed is displayed in figure 4.2.1-1, together with the proton assignments, and Table 4.2.1-1 lists proton assignments for the complexes.

Comparison of aromatic protons for the free ligand (L_2) with those for the complex $\{PdMe_2(L_2)\}$ reveal the general trend of a downfield shift (of 0.2-0.3 ppm) upon coordination to palladium. This behaviour is observed for a variety of metal ions and ligands, and is illustrated for the palladium complexes investigated in this study by the examples given in Table 4.2.1-2.

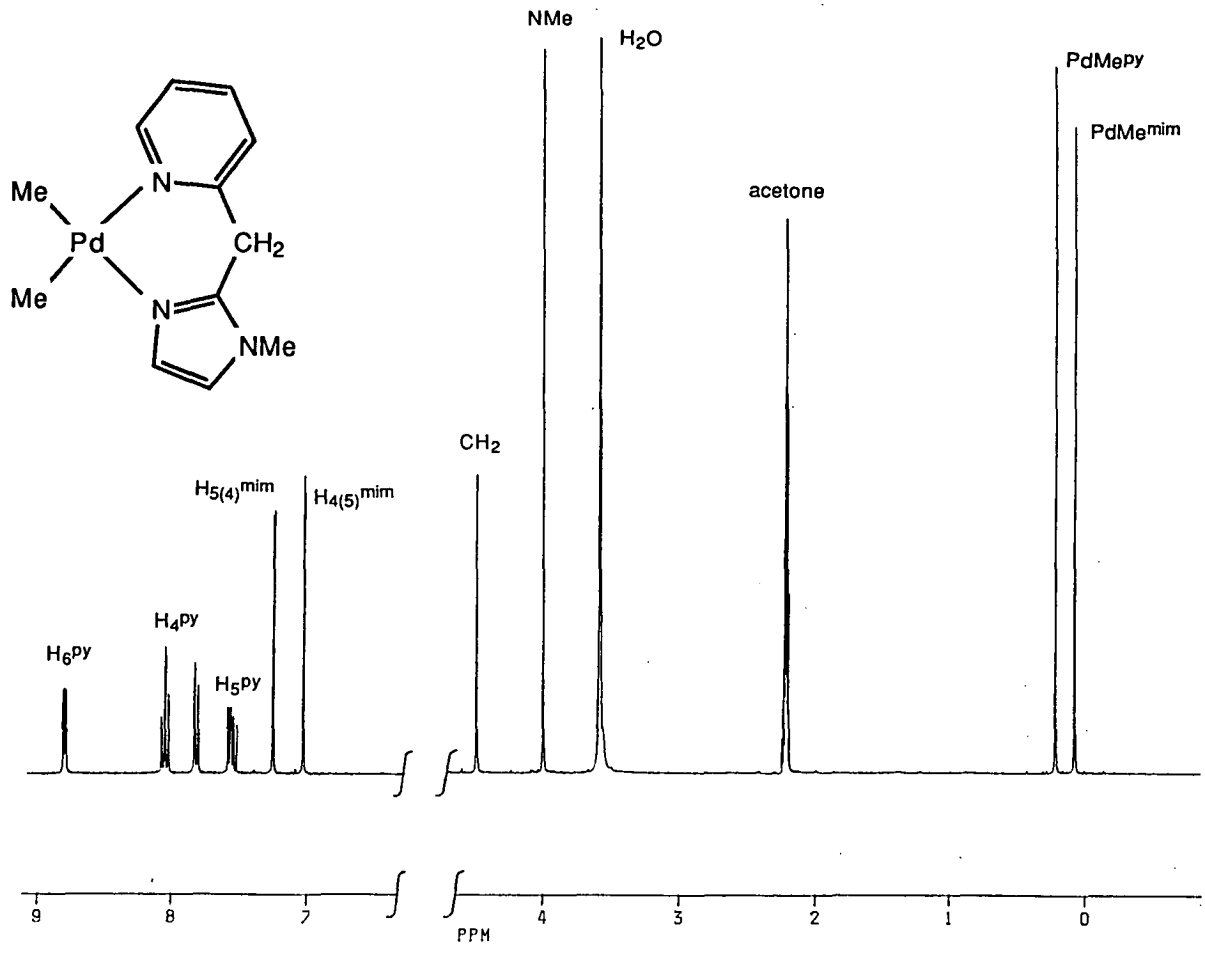
Table 4.2.1-1. ^{1}H N.M.R. Chemical Shifts for $\{PdMe_2(L_2)\}$ Complexes in Acetone-D6

Ligand L2	Chemical Shifts δ (ppm) Aromatic	Bridgehead	Pd-Me
pz_2CH_2	8.02(H_5), 7.65(H_3), 6.40(H_4)	6.71	0.11
pz_2CHMe	8.09(H_5), 7.66(H_3), 6.40(H_4)	7.16(q), 2.53(d)	0.11
pz_2CMe_2	8.66(H_5), 7.67(H_3), 6.40(H_4)	2.75	0.09
mim_2CH_2[a]	7.26($H_{4(5)}$), 6.96($H_{5(4)}$)	4.26	-0.09
mim_2CHMe	7.03($H_{4(5)}$), 6.96($H_{5(4)}$)	4.68(q), 1.70(d)	-0.02
$mim_2C{=}CH_2$	7.20($H_{4(5)}$), 7.05($H_{5(4)}$)	6.16	-0.03
$mim_2C{=}O$	7.59($H_{4(5)}$), 7.39($H_{5(4)}$)	-	0.10
py_2CH_2	8.61(H_6), 7.83(H_4), 7.64(H_3), 7.38(H_5)	4.61	0.13
py_2CHMe	8.68(H_6), 7.87(H_4), 7.58(H_3), 7.34(H_5)	5.2, 2.4	0.14
py_2CMe_3	8.78(H_6), 7.89(H_4), 7.73(H_3), 7.84(H_5)	3, 2.3	0.14
$py_2C{=}CH_2$	8.66(H_6), 7.99(H_4), 7.73(H_3), 7.49(H_5)	6.00	0.01
$pymimCH_2$	8.65(H_6), 7.90(H_4), 7.68(H_3), 7.42(H_5)	4.34	0.07,
	7.11($H_{4(5)}$), 6.88($H_{5(4)}$)		-0.07
pymimCHMe	8.76(H_6), 7.87(H_4), 7.60(H_3), 7.36(5)	4.71(q)	0.11
	7.18($H_{4(5)}$), 6.92($H_{5(4)}$)	2.14(d)	-0.03
pymimCO	8.89(H_6), 8.22($H_{3,4}$), 7.76(H_5)	-	0.12
	7.63($H_{4(5)}$), 7.32($H_{5(4)}$)		-0.01
$pymimC{=}CH_2$	8.76(H_6), 7.98(H_4), 7.78(H_3), 7.45(H_5)	6.25	0.08
	7.25($H_{4(5)}$), 7.03($H_{5(4)}$)	6.01	-0.10
$pypzCH_2$	8.69(H_6)[b], 7.97(H_4)[b], 7.70(H_3)[b], 7.51(H_5)[b]	5.71	0.14
	7.97(H_5), 7.57(H_3), 6.34(H_4)		0.08
$pzmimCH_2$	7.95(H_5), 7.60(H_3), 6.32(H_4)	5.57	0.09,
	7.11($H_{4(5)}$), 6.96($H_{5(4)}$)		-0.01
pymim	8.68(H_6), 8.10($H_{3,4}$), 7.56(H_5)	-	0.24
	7.42($H_{4(5)}$), 7.12($H_{3(4)}$)		0.05
bipy	8.87(H_6), 8.46(H_3), 8.27(H_4), 7.69(H_5)	-	0.24
phen	9.12($H_{2,9}$), 8.76($H_{4,7}$), 8.17($H_{5,6}$),	-	0.38
	8.04($H_{3,8}$)		

(a) recorded in DMSO-D6

(b) pyridine ring

Figure 4.2.1-1. ^{1}H NMR of {$PdMe_2(pymimCH_2)$} in Acetone-D6.



Further, examination of the PdMe chemical shift for complexes containing symmetrical ligands, *i.e.* those ligands which contain identical donor groups (*e.g.* py_2CH_2, pz_2CH_2), reveals that methyl groups *trans* to pyridine have essentially the same chemical shift as groups *trans* to pyrazole, with those *trans* to pyrazole occurring approximately 0.03 ppm further upfield. This is to be compared with methyl groups *trans* to *N*-methylimidazole which are shifted *ca.* 0.15 ppm further upfield from methyl groups *trans* to either pyrazole or pyridine.

This behaviour allows assignment of PdMe chemical shifts for complexes containing asymmetric ligands, *e.g.* $pymimCH_2$ or $pzmimCH_2$, and leads to assignment of PdMe *trans* to mim upfield from PdMe *trans* to pyrazole or pyridine groups. However, assignment of PdMe for mixed pyrazole/pyridine based ligands, *e.g.* $pypzCH_2$, is not as clear due to the small separation found (*vide supra*), although

Table 4.2.1-2 Chemical Shifts for Selected {$PdMe_2(L_2)$} Complexes and the Corresponding Free Ligand.

Ligand	Chemical Shift δ (ppm) Free Ligand				Complex				Pd-Me
	H_3	H_4	H_5	H_6	H_3	H_4	H_5	H_6	
pz_2CH_2	7.47	6.27	7.85	-	7.65	6.40	8.02	-	0.11
py_2CHMe	7.46	6.25	7.80	-	7.66	6.40	8.09	-	0.11
pz_2CMe_2	7.47	6.24	7.58	-	7.67	6.40	8.16	-	0.09
py_2CH_2	7.23	7.68	7.19	8.49	7.64	7.88	7.38	8.61	0.12
py_2CHMe	7.33	7.67	7.17	8.50	7.58	7.87	7.34	8.68	0.14
py_2CMe_2	7.21	7.65	7.15	8.49	7.73	7.89	7.34	8.78	0.14
mim_2CHMe		6.94	6.80			7.03	6.96		-0.02
mim_2CH_2[a]		6.94	6.77			7.26	6.96		-0.09
$mim_2C{=}CH_2$		7.09	6.94			7.20	7.05		-0.03

(a) recorded in DMS0-D6

assignment of PdMe *trans* to pyrazole upfield from PdMe *trans* to pyridine is tentatively suggested.

The complexes also displayed interesting variable temperature behaviour, and to facilitate discussion results are reported according to the bridgehead functionalisation, *i.e.* within the categories methanes (R_2CH_2), ethanes (R_2CHMe), and propanes (R_2CMe_2). For reasons which will become apparent, emphasis is placed on complexes which contain symmetrical pyrazole and pyridine based alkanes.

(a) Methane-Bridged Ligands, R_2CH_2

The majority of complexes studied within this category gave sharp well resolved spectra at ambient temperature, *e.g.* $\{PdMe_2(pymimCH_2)\}$ in figure 4.2.1-1. The ambient temperature spectrum of $\{PdMe_2(py_2CH_2)\}$ also exhibited a well resolved aromatic region, although the resonance arising from the bridgehead protons was broad, figure 4.2.1-2. On warming the solution this resonance sharpened to give the normally observed singlet (as for $\{PdMe_2(pymimCH_2)\}$ in figure 4.2.1-1), or could be resolved on cooling to give two doublets (with ^2J=13.1 Hz), figure 4.2.1-3.

Figure 4.2.1-2. ^1H NMR of $\{PdMe_2(py_2CH_2)\}$ in Acetone-D6.

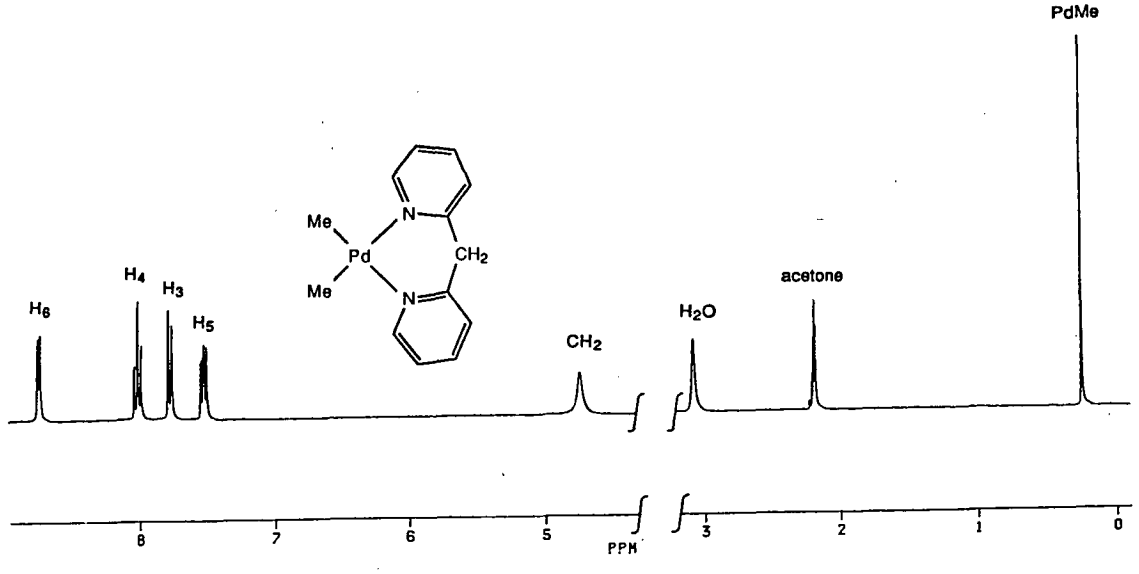
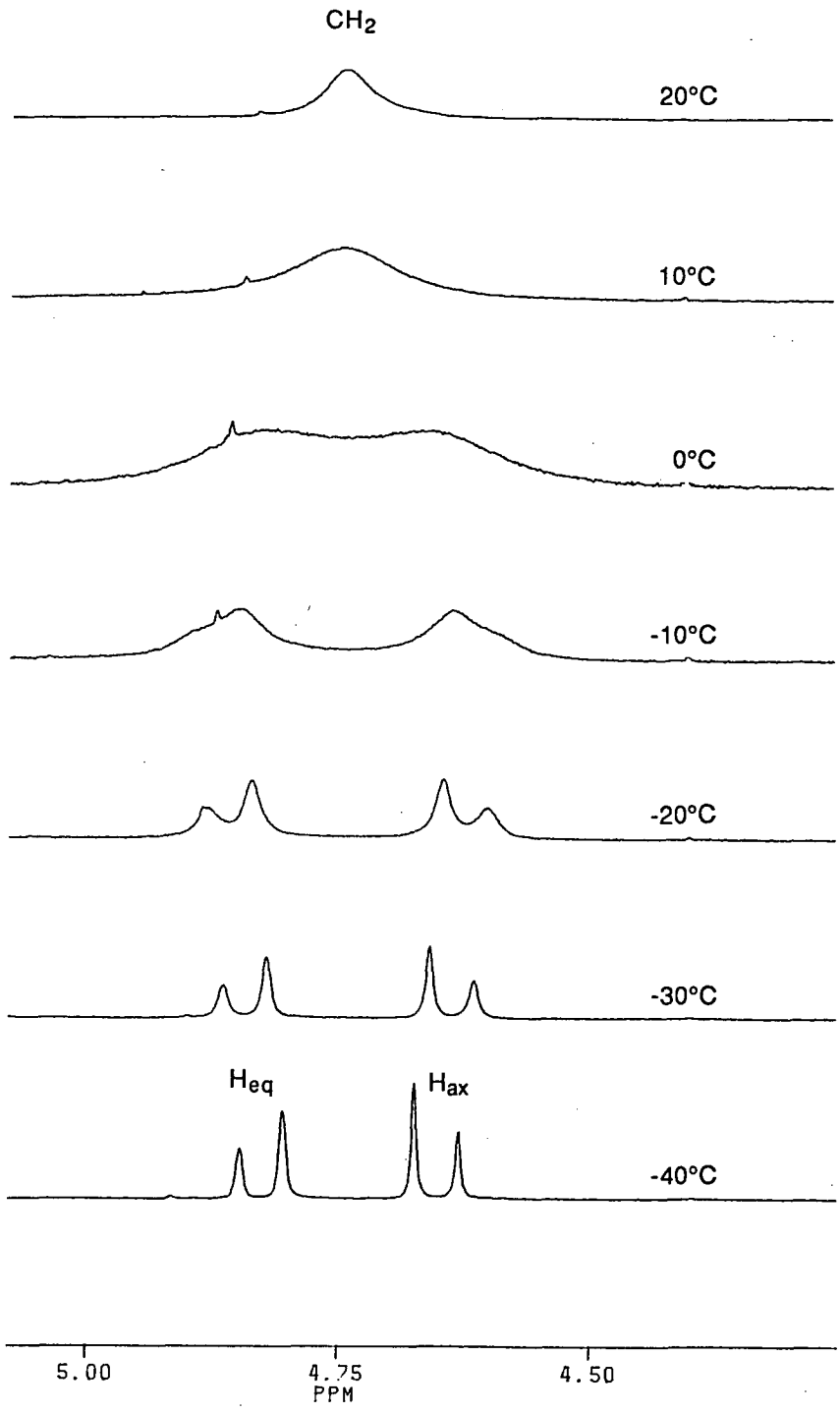


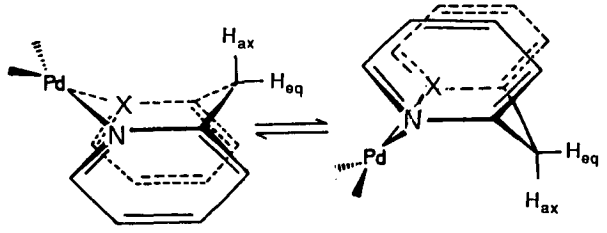
Figure 4.2.1-3. Variable Temperature ^1H NMR of $\{PdMe_2(py_2CH_2)\}$ in Acetone-D6 (Bridgehead Region).



Complexes of this type are expected to have a 'boat' conformation for the PdNCCCN ring, *e.g.* as in $\{PdCl_2(py_2(OH)_2)\}$,[3] and thus the N.M.R. behaviour is indicative of boat to boat ring inversion of the six membered chelate ring, figure 4.2.1-4 (X=N). Similar behaviour has been reported previously for some palladium(II)

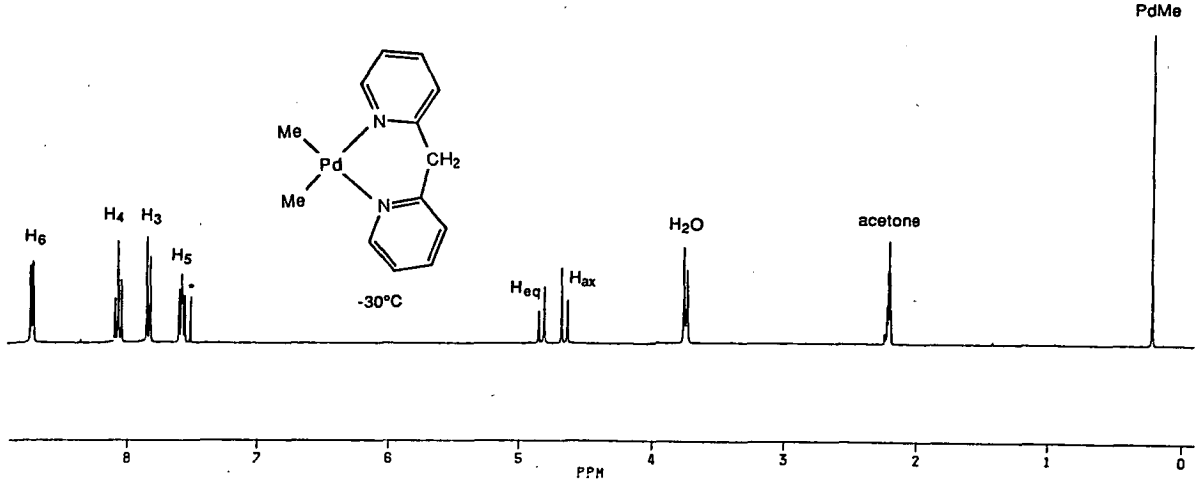
complexes containing the cyclopalladated ligand 2-benzylpyridine, figure 4.2.1-4 (X=C).[4,5]

Figure 4.2.1-4.



It is generally accepted that an axial geminal proton appears at higher field compared with an equatorial proton due to the shielding of the former by the adjacent aromatic rings.[5] Thus, in the low-temperature limiting spectrum of $\{PdMe_2(py_2CH_2)\}$, figure 4.2.1-5, the upfield doublet has been assigned to the axial proton, and the downfield doublet assigned to the equatorial proton.

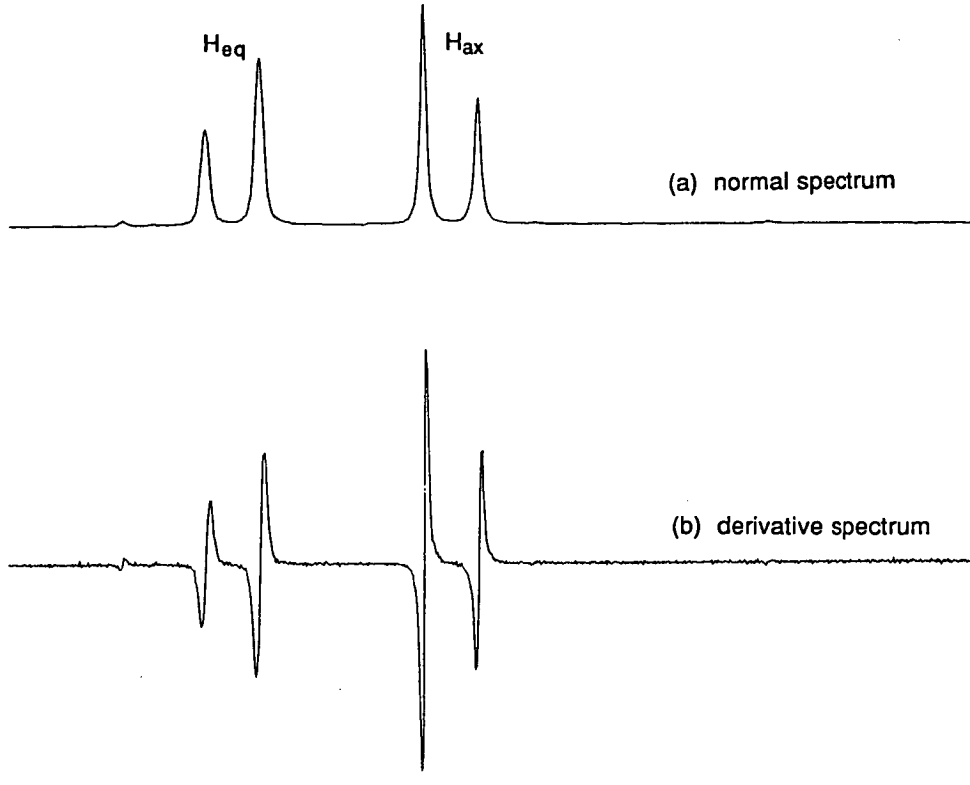
Figure 4.2.1-5. ^1H NMR of $\{PdMe_2(py_2CH_2)\}$ in Acetone-D6 at -30°C.



Further support for this interpretation is obtained from the observation that the low field doublet is broader and less resolved than the high field doublet, figure 4.2.1-6a. Broadening of the equatorial signal is clearly portrayed in the derivative spectrum, figure 4.2.1-6b. This broadening has been ascribed to the quadrupole effect of the

pyridine nitrogen,[5] since, in $\{PdMe_2(py_2CH_2)\}$, the latter is *trans* to the equatorial and *cis* to the axial protons, figure 4.2.1-4.

Figure 4.2.1-6. ^1H NMR of $\{PdMe_2(py_2CH_2)\}$ in Acetone-D6 at -30°C and its Derivative Spectrum



Investigation of the temperature dependence of other dimethylpalladium(II) complexes containing methane bridged ligands revealed analogous behaviour for $\{PdMe_2(pz_2CH_2)\}$ (coalescence temperature=-10°C, ^2J=14.1 Hz) and $\{PdMe_2(pypzCH_2)\}$ (coalescence temperature=-40°C, ^2J=14.4 Hz). However, anomalous behaviour was observed for complexes with ligands containing one or two *N*-methylimidazole groups, *e.g.* $\{PdMe_2(pymimCH_2)\}$.

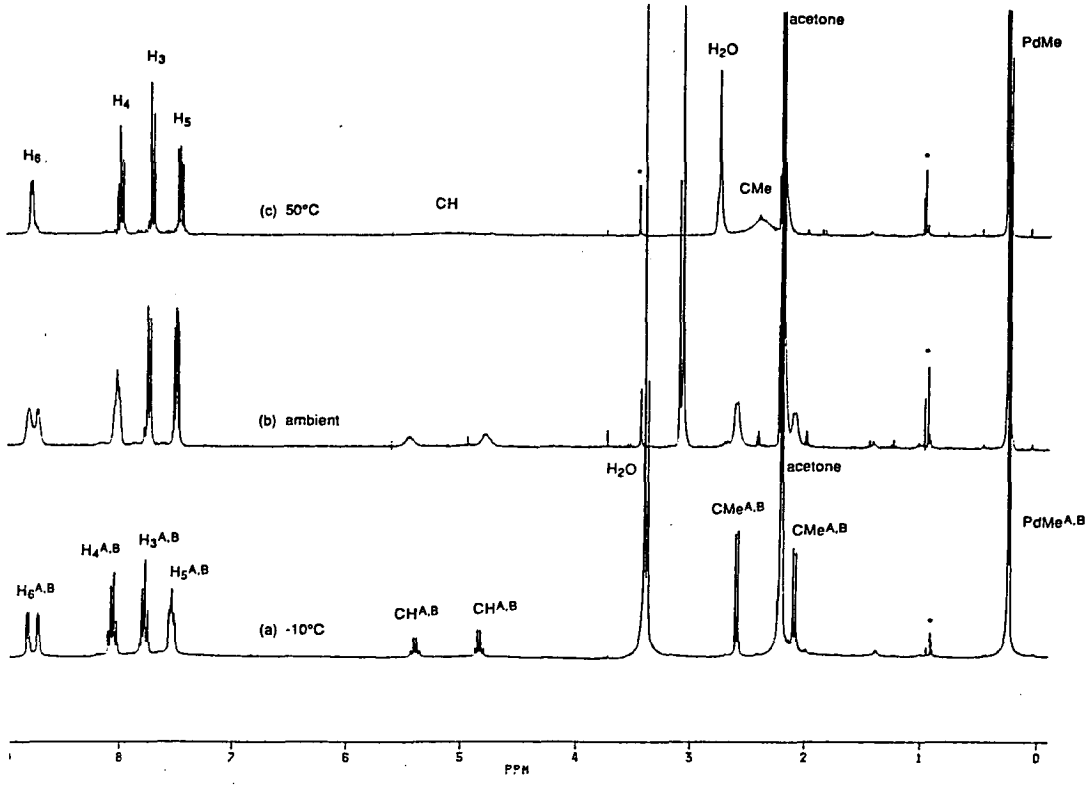
For these complexes the ^1H N.M.R. spectra were sharp and well resolved for all resonances within the temperature range 40→-70°C. The appearance of the bridgehead protons as a sharp singlet over the whole of this range, with no broadening evident, is indicative of facile boat to boat ring inversion. In these complexes the rate

of conformational exchange is fast on the N.M.R. time scale and neither conformer is observed, giving an average spectrum. The possibility that the complexes are 'frozen' in one conformation can be discounted due to the appearance of only one singlet arising from the bridgehead protons instead of the expected two, or, with coupling, a pair of doublets.

(b) Ethane-Bridged Ligands, R_2CHMe

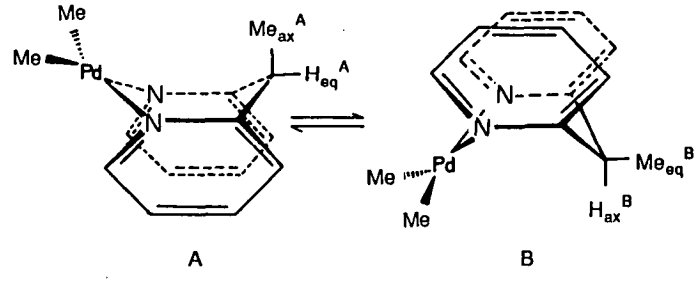
As was found for $\{PdMe_2(py_2CH_2)\}$, the ambient temperature spectrum of $\{PdMe_2(py_2CHMe)\}$ displayed broad poorly resolved resonances assignable to the bridgehead protons, although, in addition, the aromatic (pyridine) resonances were also broad and the spectrum displayed a doubling of all bridgehead and some aromatic protons, figure 4.2.1-7b. Warming this solution to *ca.* 50°C resulted in coalescence of the aromatic and aliphatic protons to give a single pyridine environment, and a single, *albeit* broad, bridgehead environment, figure 4.2.1-7c. Cooling the solution to -10°C gave a spectrum similar to that observed at ambient temperature but with all resonances well resolved and with the PdMe resonance split into a doublet, figure 4.2.1-7a.

Figure 4.2.1-7. Variable Temperature ^1H NMR of $\{PdMe_2(py_2CHMe)\}$ in Acetone-D6.



This behaviour is consistent with boat to boat ring inversion of the six membered chelate ring, as discussed above for {$PdMe_2(py_2CH_2)$}, although in this instance the rate of exchange between the conformers is sufficiently slow at room temperature to allow detection of both isomers on the N.M.R. time scale, figure 4.2.1-8, with the isomers present in *ca.* 1:1 ratio.

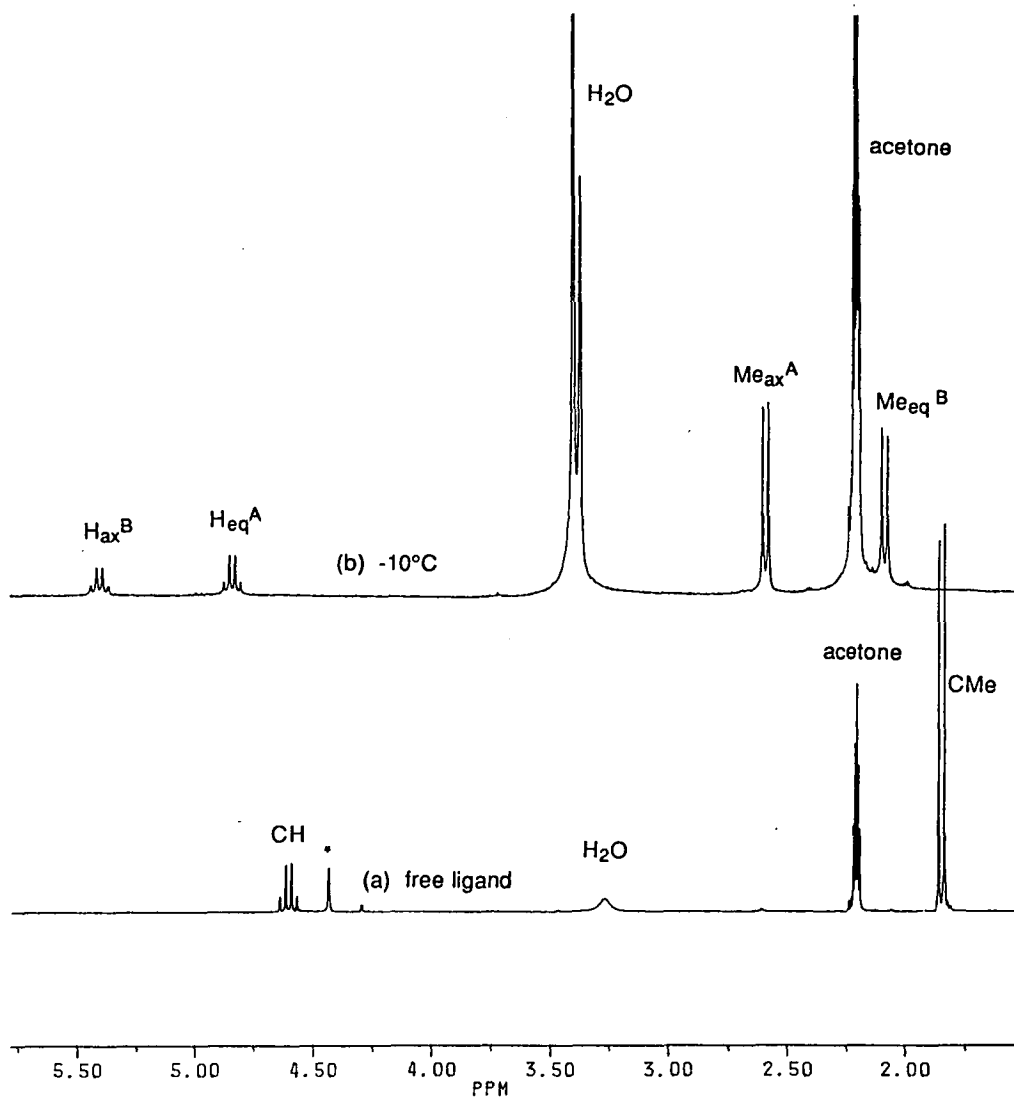
Figure 4.2.1-8.



In the low temperature limiting spectrum, assignment of pyridine and PdMe resonances to a particular isomer has not been attempted, although assignment of bridgehead protons has been possible. Figure 4.2.1-9 displays the free ligand spectrum of py_2CHMe, together with the low temperature spectrum (-10°C) of {$PdMe_2(py_2CHMe)$} within the range 1-6 ppm. Assignments are shown in full, with the justification of assignments outlined below.

Both coupling constant values and homonuclear decoupling experiments indicate resonances labelled H_{eq}^{A} and Me_{ax}^{A} correspond to one particular isomer, while resonances H_{ax}^{B} and Me_{eq}^{B} correspond to the other. Further, the protons H_{eq}^{A} and Me_{eq}^{B} display downfield shifts of *ca* 0.25 ppm compared with the free ligand, commensurate with that normally observed upon coordination of a ligand to a metal ion. This is to be compared with the H_{ax}^{B} and Me_{ax}^{A} protons which are shifted 0.80 ppm and 0.75 ppm downfield compared with the free ligand. Also, it should be noted, that with this assignment H_{ax}^{B} displays a downfield shift, while H_{ax} in {$PdMe_2(py_2CH_2)$} is shifted upfield (*vide supra*).

Figure 4.2.1-9. ^1H NMR of {$PdMe_2(py_2CHMe)$} and free py_2CHMe in Acetone-D6.

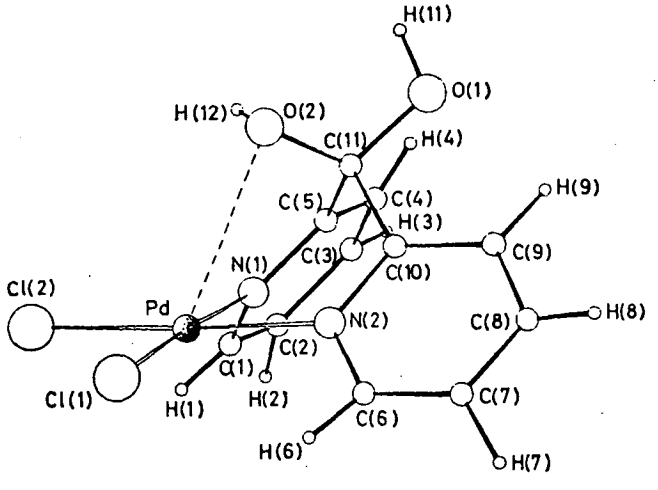


Resonance $Me_{ax}{}^A$ has been assigned to isomer A, *i.e.* that isomer containing the bridgehead methyl group in an axial orientation, figure 4.2.1-8. The basis of this assignment is the observed downfield shift of the methyl protons in the N.M.R. spectrum. This shift is a result of the close spatial proximity of the methyl group to the palladium centre, perhaps forming an agostic interaction;[6] similar deshielding of protons adjacent to palladium has been reported previously.[5-7] Consistent with this assignment is the observation that the corresponding bridgehead proton in an equatorial orientation *i.e.* $H_{eq}{}^A$, is relatively unperturbed, compared with the free ligand.

Thus, following the assignments above, quartet H_{ax}^{B} and doublet Me_{eq}^{B}, are assigned to isomer B, *i.e.* that isomer containing the bridgehead methyl group in an equatorial orientation. (This interpretation is supported by the observation that Me_{eq}^{B} is relatively unperturbed compared with the free ligand, as would be expected. The downfield shift of H_{ax}^{B} is readily rationalised by considering the steric crowding that occurs between an equatorial bridgehead methyl group and the pyridine H_3 protons, figure 4.2.1-8. To relieve this crowding increased puckering of the six membered chelate ring may occur, resulting in the placement of H_{ax}^{B} close to the palladium centre. This proton is thus deshielded to give the observed downfield shift in the N.M.R. spectrum.

The structural features outlined above may be readily confirmed upon construction of a molecular model of $\{PdMe_2(py_2CHMe)\}$, or upon inspection of the crystal structure of a close analogue, *e.g.* $\{PdCl_2(py_2C(OH)_2)\}$ in figure 4.2.1-10.[3] For example, for $\{PdCl_2(py_2C(OH_2)\}$ the Pd···O(2) distance is 2.824(6)Å, which is less than the expected sum of the Van der Waals radii (*ca.* 3.1Å). Replacement of O(2) by Me_{ax}^{A} may also give a Pd···Me_{ax}^{A} distance less than the sum of the Van der Waals radii, and may result in the formation of a weak agostic interaction. Similarly, the expected steric interactions between an equatorial methyl group and the H_3 pyridine protons of $\{PdMe_2(py_2CHMe)\}$ is illustrated by the proximity of O(2) to the $H_{(4)}$ and $H_{(9)}$ protons within $\{PdCl_2(py_2C(OH)_2)\}$.

Figure 4.2.1-10.



The analogous complex {$PdMe_2(pz_2CHMe)$}, containing the symmetrical pyrazole based ligand pz_2CHMe, also displayed temperature dependent inversion of the six membered chelate ring. In this case, the rate of inversion at ambient temperature was fast and an average environment was observed, figure 4.2.1-11b. Cooling this solution to -30°C, however, gave a fully resolved spectrum exhibiting two conformational isomers, figure 4.2.1-11a; a pictorial representation of these isomers is given in figure 4.2.1-12.

Figure 4.2.1-11. Variable Temperature ^1H NMR of {$PdMe_2(pz_2CHMe)$} in Acetone-D6.

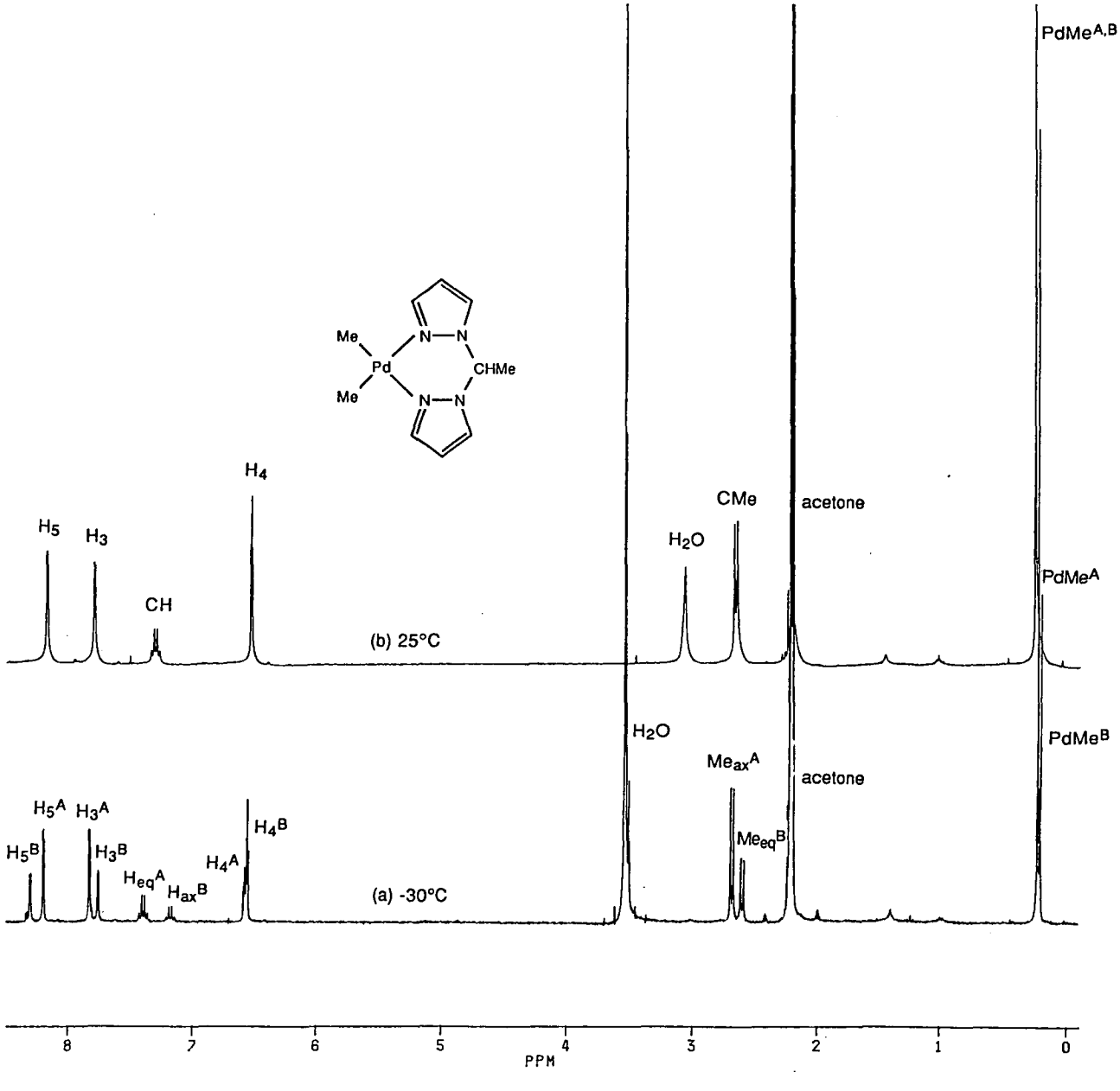
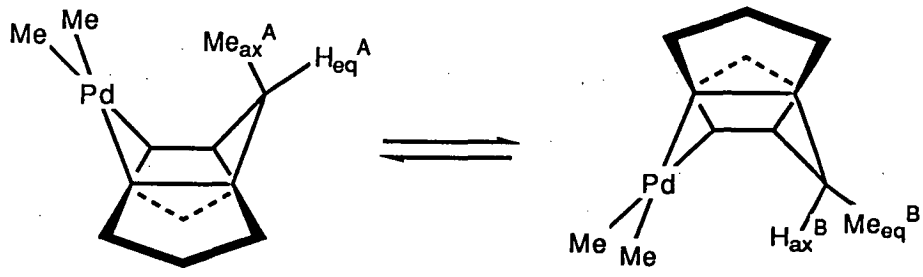


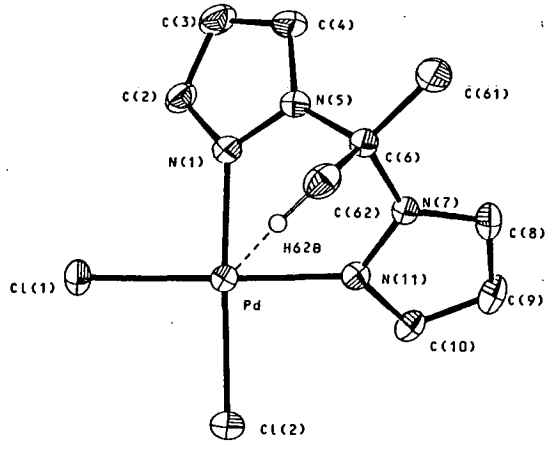
Figure 4.2.1-12.



Conformer A Conformer B

In contrast to {$PdMe_2(py_2CHMe)$}, the low temperature limiting spectrum of {$PdMe_2(pz_2CHMe)$} displayed a preference for one conformational isomer over the other, figure 4.2.1-11a, with the ratio A:B equal to 2:1, and unambiguous assignment of all protons within each isomer is clearly possible. However, in this instance, resonances for both isomers appeared at expected positions, *i.e.* the observed downfield shifts were of a similar magnitude to that frequently seen upon coordination of a ligand to palladium. This is readily understood on examination of molecular models and the crystal structure of {$PdCl_2(pz_2CMe_2)$}, figure 4.2.1-13, following the approach discussed for {$PdCl_2(py_2C(OH)_2$}.

Figure 4.2.1-13.[10]



Examination of molecular models reveals that, in contrast to {$PdMe_2(py_2CHMe)$}, steric clash between an equatorial bridgehead methyl group and the aromatic ring protons, in this case the H_5 protons, is reduced. Thus, assignment of the bridgehead protons (H_{eq}^A and H_{ax}^B) is based upon the same arguments invoked to assign the bridgehead protons in the analogous complex {$PdMe_2(pz_2CH_2)$}, *i.e.* since an axial geminal proton appears at higher field compared with an equatorial proton,[5] the major species displayed in the low temperature spectrum is assigned to conformer A, and the minor to conformer B.

The presence of conformer A in preference to conformer B (*ca.* 2:1 ratio) is consistent with this assignment, as structural[8] and solution state studies[9] suggest that in similar complexes the bridgehead group of greatest steric demand is positioned over the metal in an axial orientation, rather than the relatively more sterically hindered equatorial position.

A similar approach for {$PdMe_2(py_2CHMe)$} would also suggest a preference for conformer A over conformer B, as for {$PdMe_2(pz_2CHMe)$}, but for {$PdMe_2(py_2CH_2)$} other factors are present. In addition to stronger $Me_{eq}^B \cdots H_3$ (pyridine) interactions, favouring A over B, conformer A places the Me_{ax}^A group much closer to the palladium centre than Me_{ax}^A for {$PdMe_2(pz_2CHMe)$}. The closer proximity of Me_{ax}^A to the palladium centre in {$PdMe_2(py_2CHMe)$} compared with {$PdMe_2(pz_2CHMe)$} is reflected in the increased deshielding experienced by Me_{ax}^A, relative to Me_{eq}^B, in the former complex compared with the latter. This is consistent with results of Deeming *et. al.*,[7] who reported that the deshielding experienced by a proton close to the palladium centre increases with decreasing Pd···H distances†.

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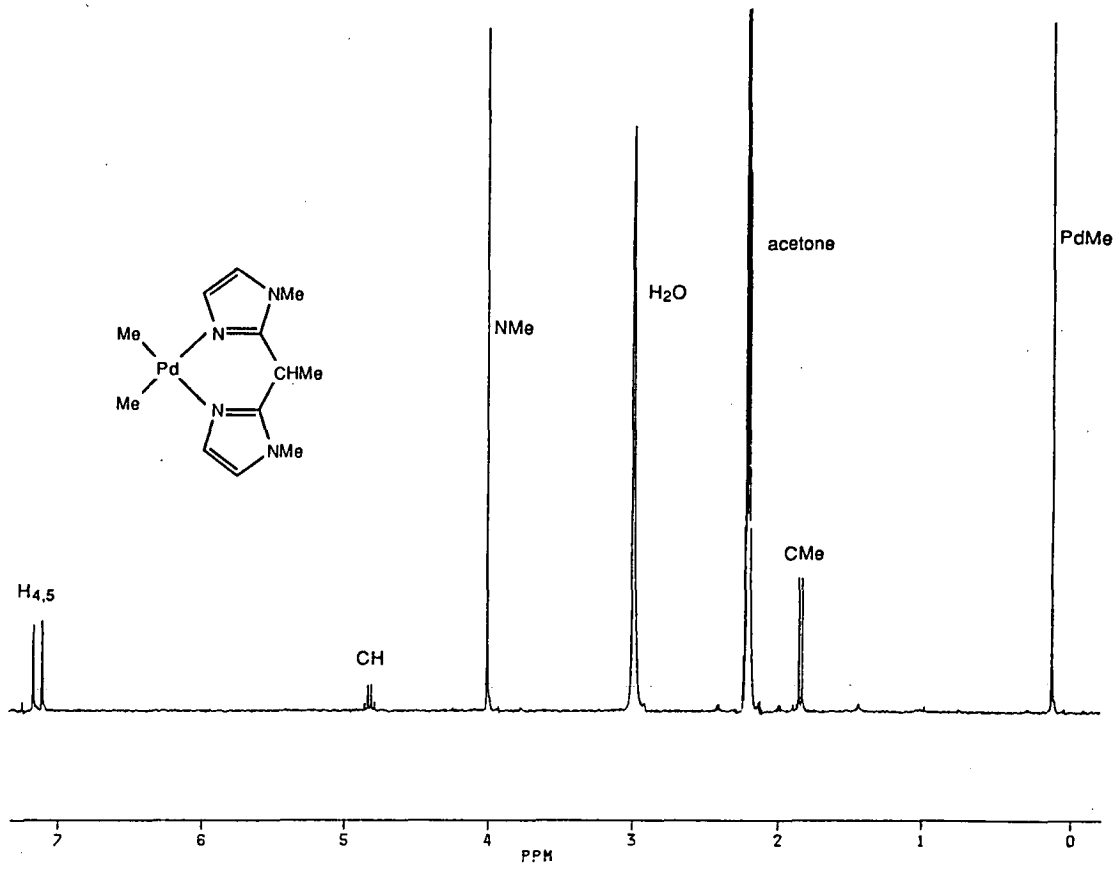
† Further support for the closer proximity of Me_{ax}^A to the palladium centre in {$PdMe_2(py_2CHMe)$} compared with {$PdMe_2(pz_2CHMe)$} is obtained upon examination of the crystal structures for {$PdCl_2(py_2C(OH)_2)$}, figure 4.2.1-10, and {$PdCl_2(pz_2CMe_2)$}, figure 4.2.1-13. The bridgehead-palladium distance for the former being 2.824(6)Å (Pd···O(2)), while for the latter it is 3.296Å (Pd···C(62)).

The attainment of a 1:1 ratio for conformers A and B in {$PdMe_2(py_2CHMe)$} tends to suggest that the agostic interaction formed, *i.e.* Pd····$Me_{ax}{}^{A}$, is destabilising. The destabilising nature of Pd····HC interactions has been reported previously by Deeming *et. al.*[7]

Spectra of the complexes {$PdMe_2(mim_2CHMe)$} and {$PdMe_2(pymimCHMe)$} within the temperature range +35→-60°C exhibited well resolved resonances for all protons, including bridgehead protons which appeared as well defined quartets and doublets, *e.g.* figure 4.2.1-14. This behaviour is indicative of the formation of a preferred conformation which does not readily undergo boat to boat interconversion.

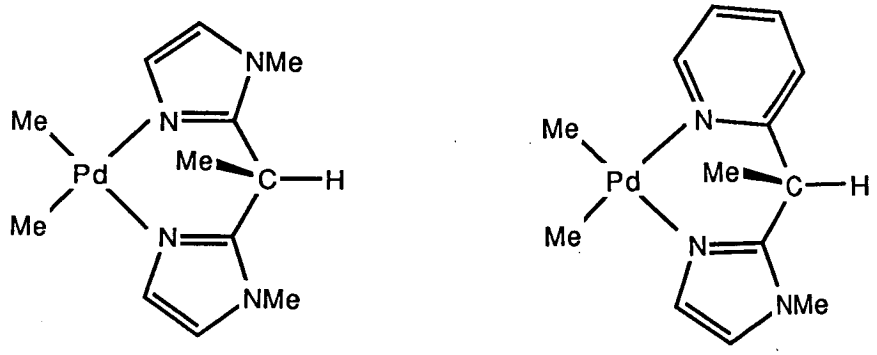
Figure 4.2.1-14. ^1H NMR of {$PdMe_2(mim_2CHMe)$} in Acetone-D6.



Examination of molecular models reveals that for these complexes acute steric hindrance occurs between an equatorial bridgehead methyl group and the adjacent *N*-methyl groups of imidazole. Thus, based on this, it is proposed that the preferred

isomer is that which contains the bridgehead methyl group in the sterically less hindered axial position, figure 4.2.1-15.

Figure 4.2.1-15.



(c) Propane-bridged ligands, R_2CMe_2.

Ambient temperature spectra of the complexes $\{PdMe_2(pz_2CMe_2)\}$ and $\{PdMe_2(py_2CMe_2)\}$ exhibited a single well resolved aromatic environment, and for $\{PdMe_2(pz_2CMe_2)\}$ a single bridgehead environment, figure 4.2.1-16b. The spectrum of $\{PdMe_2(py_2CMe_2)\}$, on the other hand, displayed two broad resonances assignable as the bridgehead methyl groups, figure 4.2.1-17b. Cooling the solutions resulted in splitting of the bridgehead resonance for $\{PdMe_2(pz_2CMe_2)\}$, figure 4.2.1-16a, and resolution of the resonances for $\{PdMe_2(py_2CMe_2)\}$, figure 4.2.1-17a, to give two sharp singlets. This behaviour is indicative of boat to boat ring inversion of the six membered chelate ring, as discussed above.

The low temperature limiting spectrum of $\{PdMe_2(py_2CMe_2)\}$, figure 4.2.1-17a, is readily assigned on the basis of arguments outlined above for $\{PdMe_2(py_2CHMe)\}$. Thus, the downfield bridgehead resonance (at *ca.* 3 ppm) is assigned to the axial methyl group, and the upfield resonance is assigned to the equatorial methyl group. Further, it is interesting to note that for $\{PdMe_2(py_2CMe_2)\}$ the equatorial and axial methyl resonances are separated by 0.75 ppm, while for $\{PdMe_2(py_2CHMe)\}$ the methyl resonances of the two conformers are separated by 0.50 ppm. The increased separation for $\{PdMe_2(py_2CMe_2)\}$ is perhaps a

Figure 4.2.1-16. Variable Temperature ^1H NMR of $\{PdMe_2(pz_2CMe_2)\}$ in Acetone-D6.

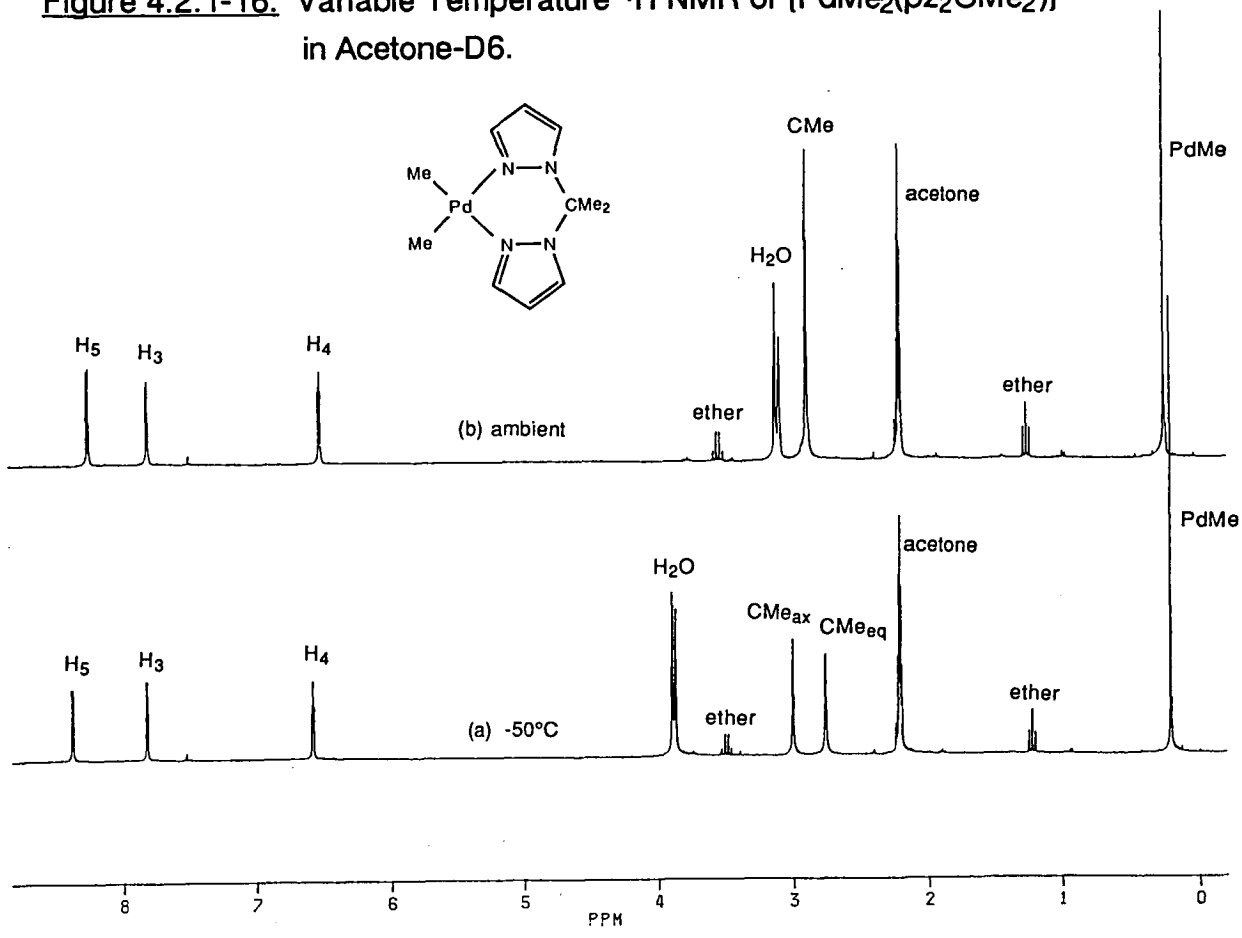
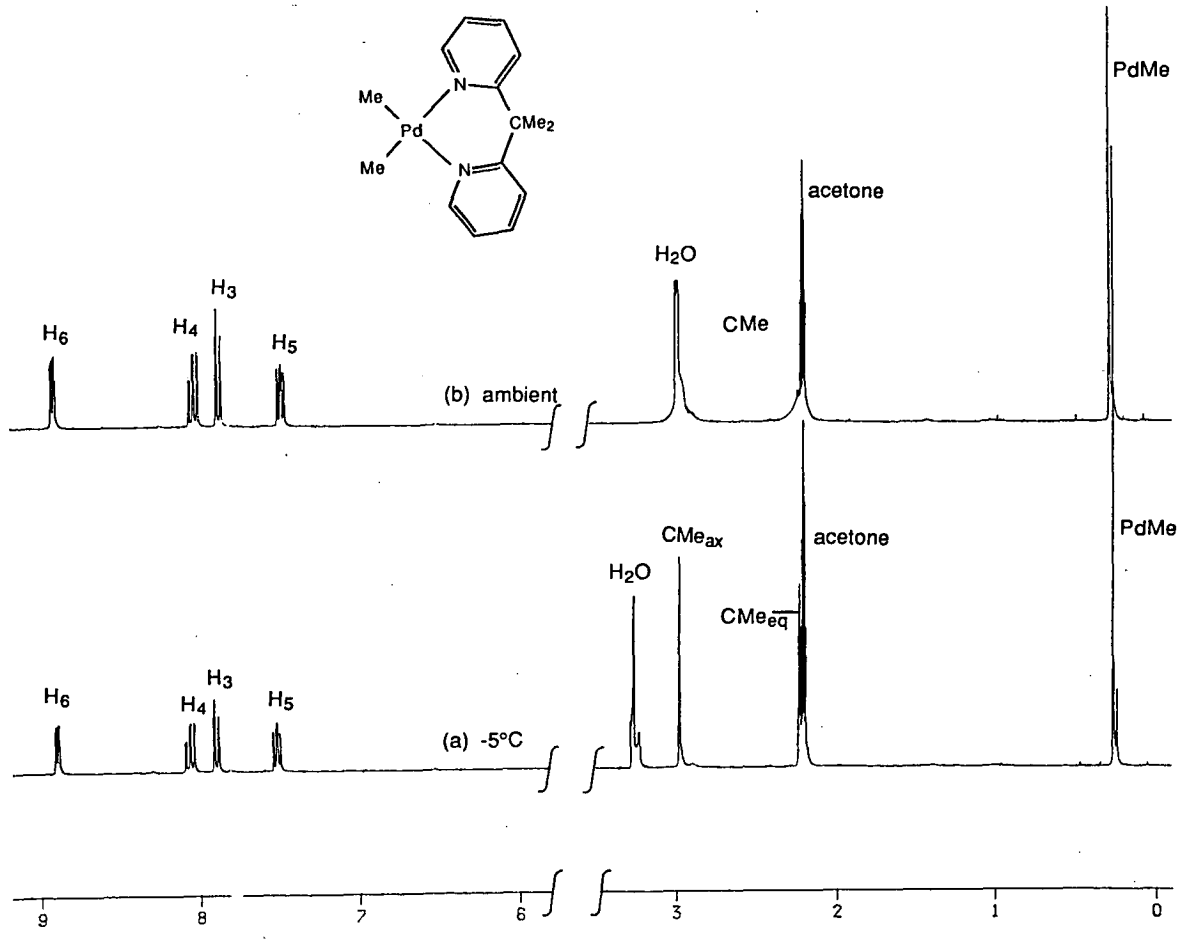


Figure 4.2.1-17. Variable Temperature ^1H NMR of $\{PdMe_2(py_2CMe_2)\}$ in Acetone-D6.



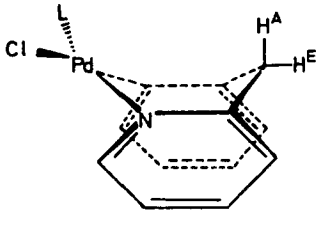
consequence of steric interactions between the equatorial methyl group and the H_3 pyridine protons, forcing the axial methyl group closer to the palladium centre. Similar arguments were applied to explain the downfield shift of the axial proton in {$PdMe_2(py_2CHMe)$} (*vide supra*).

Assignment of the bridgehead resonances for {$PdMe_2(pz_2CMe_2)$} in the low temperature spectrum is identical to that above, *i.e.* the axial methyl is assigned to the downfield resonance and the equatorial to the upfield resonance. Also, as was found on comparison of {$PdMe_2(py_2CHMe)$} with {$PdMe_2(py_2CMe_2)$}, separation of the bridgehead methyl resonances is greater for {$PdMe_2(pz_2CH_2)$} ($\Delta\delta$=0.23 ppm) compared with {$PdMe_2(pz_2CHMe)$} ($\Delta\delta$=0.08 ppm); again, this may be due to closer Pd···Me interactions within {$PdMe(pz_2CMe_2)$}.

Mechanism for Ring Inversion

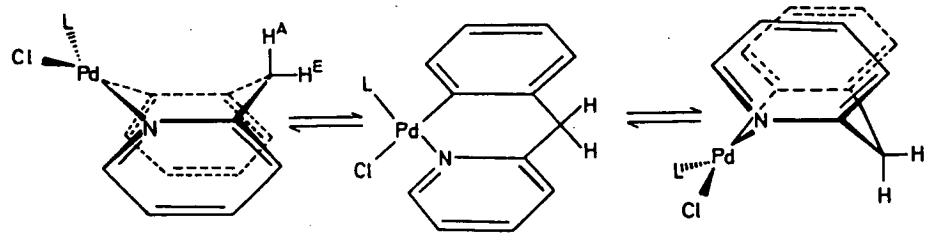
A non-dissociative mechanism has been determined by Polyakov and Ryabov[5] for the inversion of the six membered palladocycle in the closely related complexes depicted in figure 4.2.1-18. These workers found, on the basis of line shape analysis and kinetic studies, that their results could best be explained in terms of a "concerted process involving a planar transition state or intermediate without any bond breaking",[5] figure 4.2.1-19. A similar process most likely applies for the complexes reported here, and in support of this the more "planar" systems, {$PdMe_2(pz_2CH_2)$}, {$PdMe_2(pz_2CHMe)$} and {$PdMe_2(pz_2CMe_2)$}, appear to have a more facile inversion process, as expected. For example, {$PdMe_2(py_2CH_2)$} and {$PdMe_2(py_2CHMe)$} are fully resolved at -20 and -10°C respectively, while {$PdMe_2(pz_2CH_2)$} and {$PdMe_2(pz_2CHMe)$} require cooling to -40 and -30°C respectively.

Figure 4.2.1-18.



	L
(1a)	4MeO$_2$C-py
(1b)	py
(1c)	4Me-py
(1d)	3,5Me$_2$-py
(1e)	3,4Me$_2$-py
(1f)	2,4,6,Me$_3$-py
(1g)	4Me$_2$N-py
(2a)	PPh$_3$
(2b)	PMePh$_2$

Figure 4.2.1-19.



4.2.2 Monomethylhalopalladium(II) Complexes

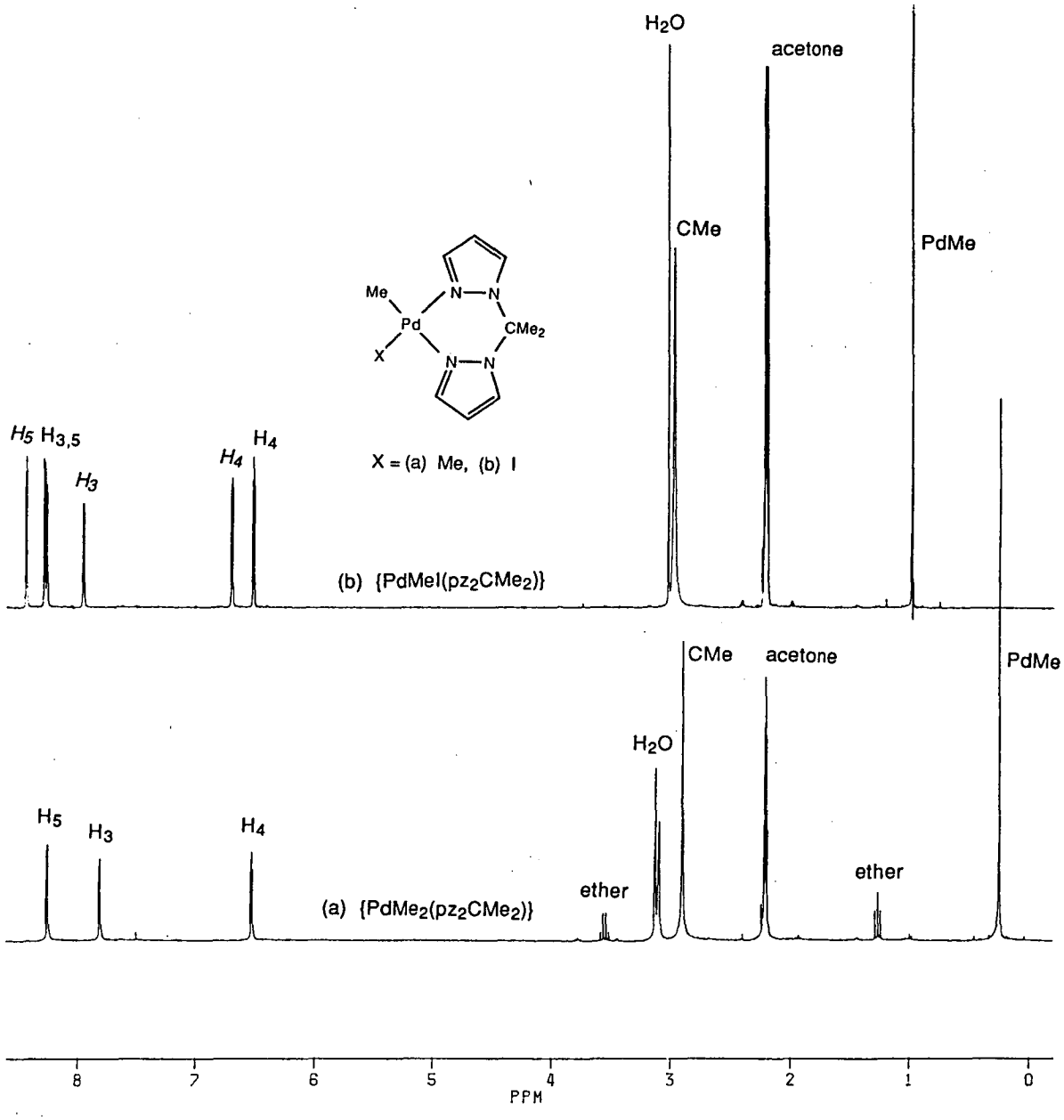
Spectra of the complexes {PdMeX(L_2)} (X=Cl, Br, I; L_2=bidentate N-donor ligands) were all recorded in acetone-D6, except for the complex {PdMeI(mim_2C=O)} which was too insoluble for spectra to be obtained in all common deuterated solvents. Proton assignments for each ring system follow directly from the observed multiplicity, ^3J coupling constants and connectivity (COSY spectrum), as discussed previously (see section 4.1).

To facilitate discussion, results are reported according to the symmetry of the bidentate ligand, *i.e.* symmetrical ligands, *e.g.* pz_2CH_2 or py_2CHMe, and unsymmetrical ligands, *e.g.* $pzimCH_2$ or $pymimC{=}CH_2$.

(a) Symmetrical Ligands, R_2C.

Two striking features noted upon comparison of the ambient temperature spectra of the complexes {PdMeX(L_2)} (X=Cl, Br, I) with the analogous dimethyl-complexes ({$PdMe_2(L_2)$}) was the complexity of the aromatic region and the downfield shift observed (*ca.* 0.6-0.7 ppm) for the PdMe resonance of the former compared with the latter. Both these features are portrayed, for example, by examination of the spectra displayed in figure 4.2.2-1b, for {PdMeI(pz_2CMe_2)}, and figure 4.2.2-1a, for {$PdMe_2(pz_2CMe_2)$}.

Figure 4.2.2-1. ^{1}H NMR of {PdMeR(pz_2CMe_2)} (R=Me, I) in Acetone-D6.



The PdMe chemical shift for a representative sample of dimethyl- and monomethylhalopalladium(II) complexes is given in Table 4.2.2-1, and reference to this table clearly illustrates the shift observed for the latter complexes compared with the former. Table 4.2.2-1 also illustrates that the magnitude of the shift, *ca.* 0.6-0.7 ppm, is similar for ligands containing pyrazole, pyridine or *N*-Methylimidazole groups, and Table 4.2.2-2 indicates that the shift is essentially independent of the halogen present.

Table 4.2.2-1 Pd-Me Chemical Shifts for Selected {$PdMe_2(L_2)$} and {$PdMeI(L_2)$} Complexes

Bridgehead function-alisation	R=pz		R=py		R=mim	
	MeIPd	Me_2Pd	MeIPd	Me_2Pd	MeIPd	Me_2Pd
R_2CH_2	0.83	0.11	0.77	0.12	0.60	-0.09
R_2CHMe	0.84	0.11	0.77	0.14	0.62	-0.02
R_2CMe_2	0.85	0.09	0.79	0.14	-	-
$R_2C{=}CH_2$	-	-	0.67	0.01	0.60	-0.03

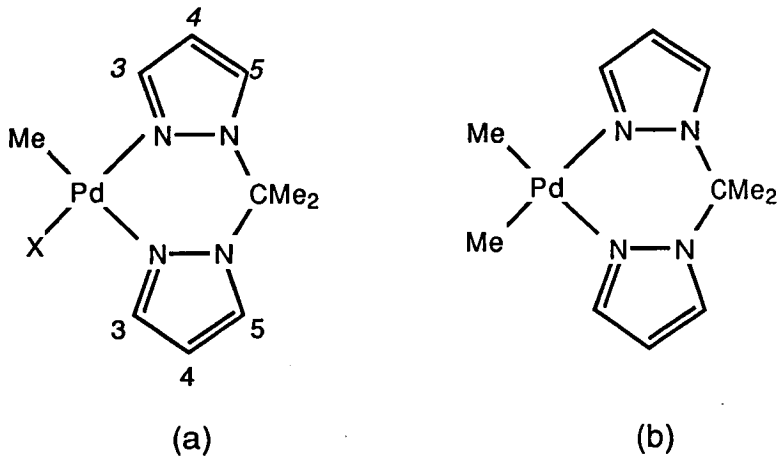
Table 4.2.2-2 Pd-Me Chemical Shifts for {$PdMeX(L_2)$} (X=Cl, Br, I and L_2=pz_2CMe_2, bipy)

Complex	X=Cl	X=Br	X=I
{$PdMeX(pz_2CMe_2)$}	0.85	0.84	0.83
{PdMeX(bipy)}	0.86	0.86	0.83

As was discussed earlier for dimethylpalladium(II) complexes of symmetrical ligands (see section 4.2.1), the relative position of the PdMe resonance is characteristic of the *trans* heterocycle present. For example, reference to Table 4.2.2-1 reveals an upfield shift in the PdMe resonance position upon progressing from pyrazole to pyridine to *N*-methylimidazole based ligands, although the shift on changing from pyrazole to pyridine is small.

Figure 4.2.2-2 displays diagrams of {$PdMeX(pz_2CMe_2)$} [(a), X=I] and {$PdMe_2(pz_2CMe_2)$} (b), and while (b) gives equivalent ring protons, (a) is observed, as expected, to give inequivalent protons. COSY spectroscopy was employed to assign protons within each ring system, and protons *trans* to methyl are given in plain text, while protons *trans* to halide are denoted by *italics*; assignment as H_3, H_4 or H_5 protons follows from the criteria discussed earlier.

Figure 4.2.2-2.

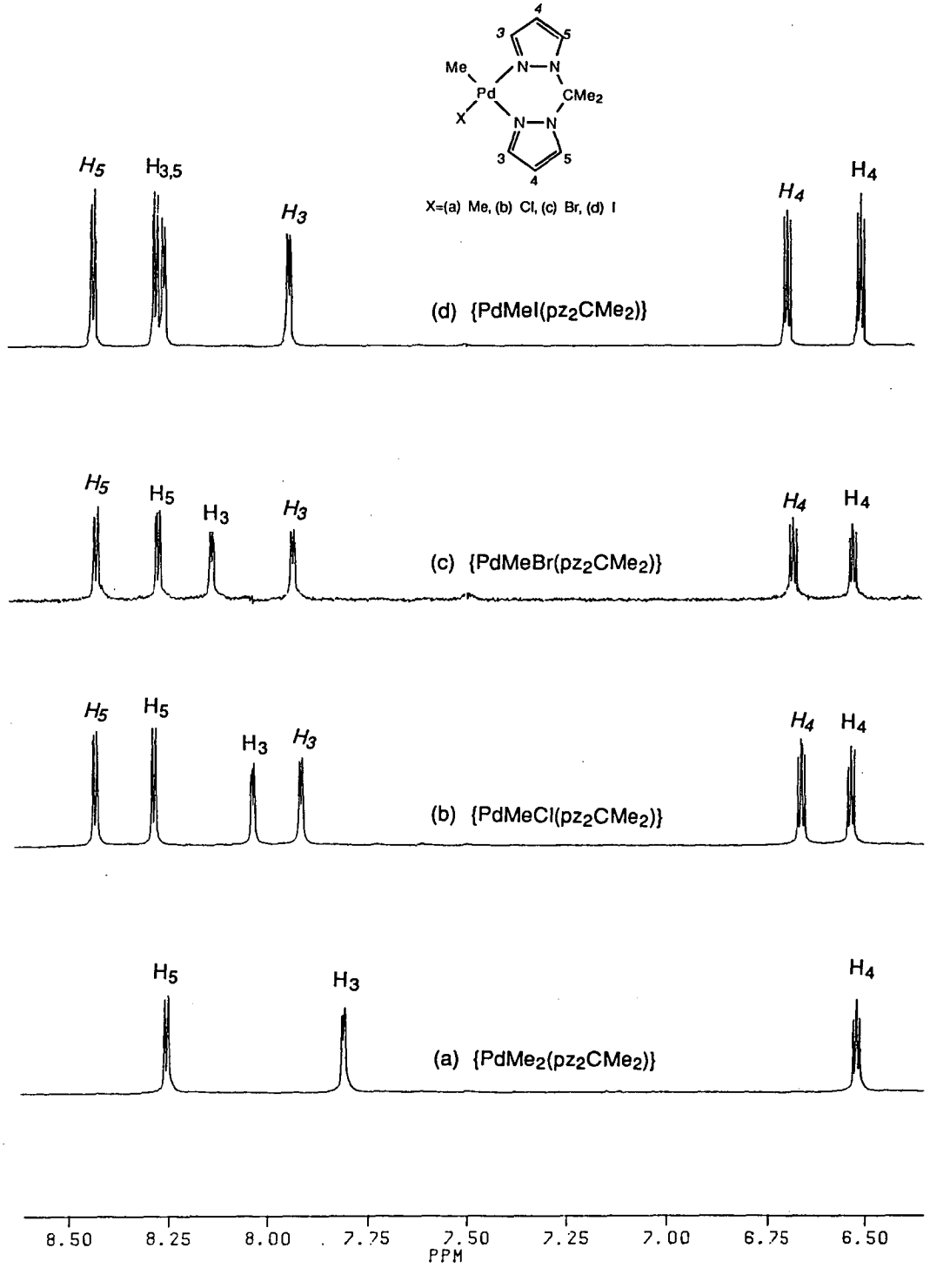


Elucidation of rings *trans* to Me and rings *trans* to X was accomplished by consideration of spectra for the series of complexes {$PdMeX(pz_2CMe_2)$} (X=Cl, Br, I), figure 4.2.2-3b,c,d, compared with the dimethyl-analogue {$PdMe_2(pz_2CMe_2)$}, figure 4.2.2-3a.

The first point to note upon examination of the spectra is that the position of the H_4 proton is essentially unchanged upon progressing from {$PdMe_2(pz_2CMe_2)$} to {$PdMeX(pz_2CMe_2)$} (X=Cl, Br, I) and this is to be compared with the H_4 proton which exhibits a downfield shift, increasing in magnitude, on passing from {$PdMe_2(pz_2CMe_2)$} to {$PdMeX(pz_2CMe_2)$}, figure 4.2.2-3. Based on this observation H_4 is assigned to the ring *trans* to X, and a full assignment follows.

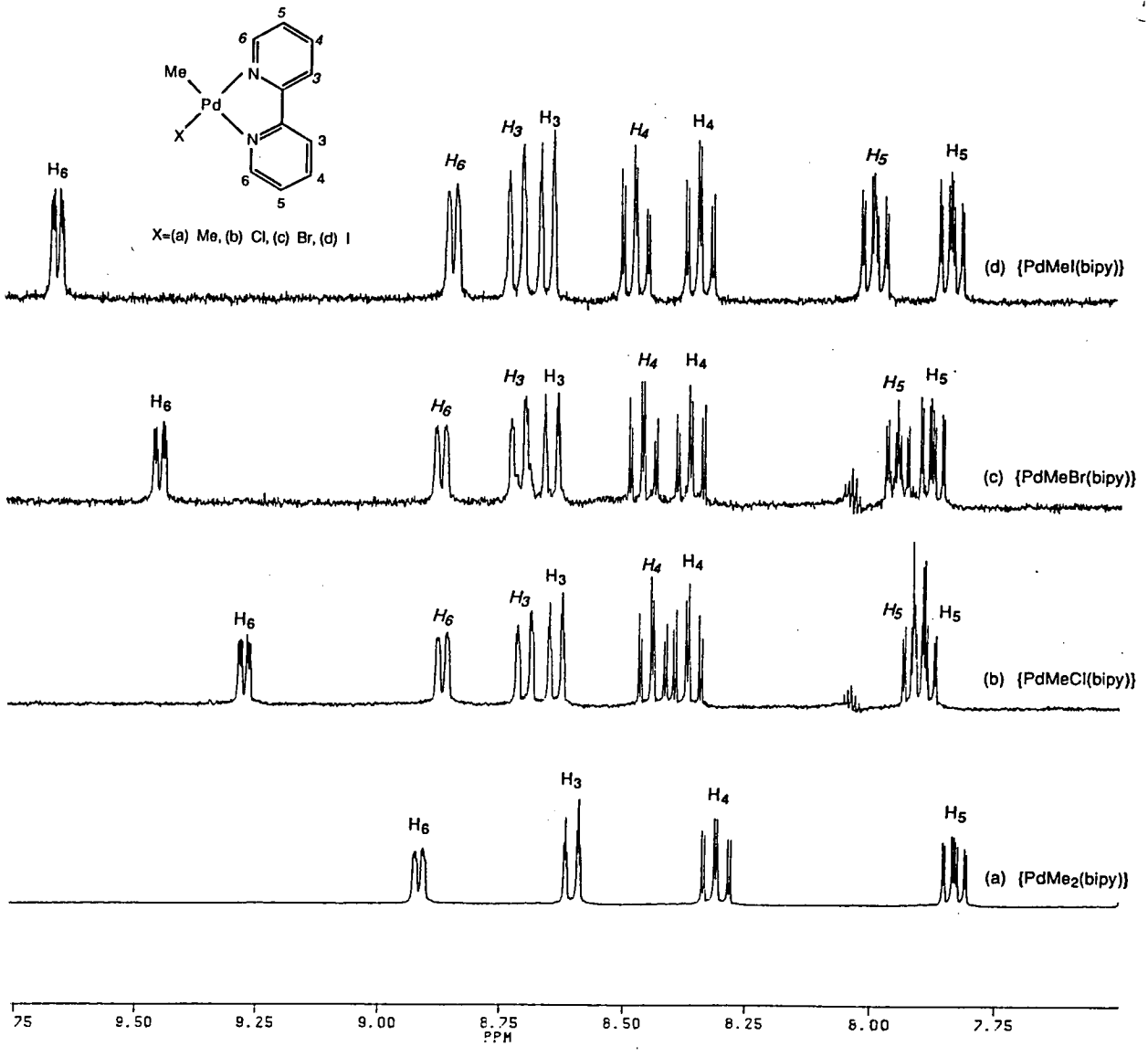
The second important feature to note is that the H_3 proton, *i.e.* the pyrazole proton adjacent to the halogeno-group and *trans* to methyl (figure 4.2.2-2), is shifted much further downfield than H_3 in the analogous complex {$PdMe_2(pz_2CMe_2)$}. Further, the magnitude of the downfield shift increases on passing from {$PdMeCl(pz_2CMe_2)$} to {$PdMeI(pz_2CMe_2)$}. This behaviour provides added support for the assignments outlined above, as the spatial proximity of H_3 to the halide anion (increasing atomic number and radius) is reflected in the observed deshielding of H_3.

Figure 4.2.2-3. ^1H NMR of {PdMeR(pz_2CMe_2)} (R=Me, Cl, Br, I) in Acetone-D6.



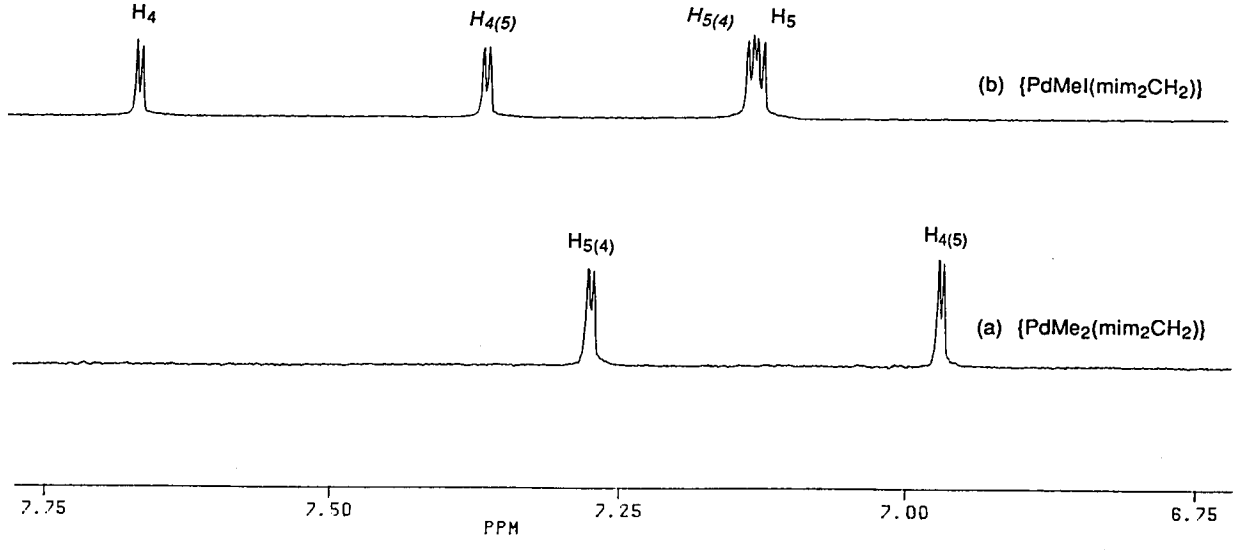
The behaviour described above is not unique to pyrazole based ligands, and spectra of {PdMeX(bipy)}(X=Cl, Br, I) may be assigned similarly, figure 4.2.2-4. Again, the most striking features are the downfield shift of the H_6 protons, which are adjacent to the halogeno-group, and the general trend of a downfield shift for protons *trans* to X (denoted by *italics*) compared with those *trans* to methyl.

Figure 4.2.2-4. ^1H NMR of {PdMeR(bipy)} (R=Me, Cl, Br, I) in Acetone-D6.



In the same manner, *N*-methylimidazole rings *trans* to methyl are readily identified by the characteristic downfield shift of the H_4 proton, and, although a complete halogeno-series has not been prepared, reference to figure 4.2.2-5 clearly illustrates deshielding of H_4 by the adjacent iodo-ligand.

Figure 4.2.2-5. ^1H NMR of {$PdMeR(mim_2CH_2)$} (R=Me, I) in Acetone-D6.



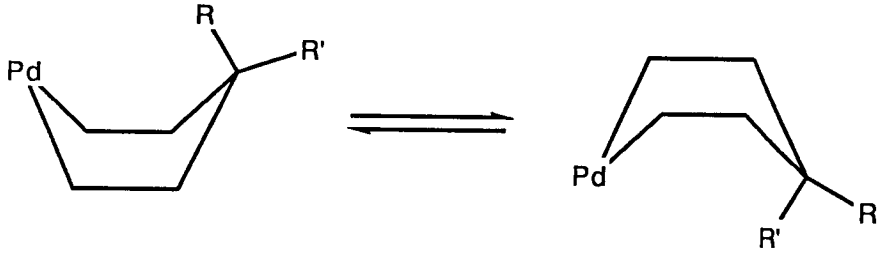
In summary, for complexes of the form {$PdMeX(L_2)$} {L_2=symmetrical bidentate ligand) the heterocyclic ring *trans* to methyl is readily identified by the large downfield shift of the H_6 (pyridine), H_3 (pyrazole) or H_4 (*N*-methylimidazole) proton, *i.e.* the proton adjacent to the halide anion. Secondly, the heterocyclic ring *trans* to iodide has all protons, except for H_6 (pyridine), H_3 (pyrazole) and H_4 (*N*-methylimidazole) downfield from the analogous protons in the ring *trans* to methyl. Generally, assignment of the proton adjacent to the halogeno-group, together with a COSY spectrum, allows full assignment of the aromatic region. Table 4.2.2-3 reports assignments for the complexes {$PdMeX(L_2)$} (X=halide, L_2=symmetrical bidentate ligands).

Table 4.2.2-3 ^{1}H Chemical Shifts for Monomethylhalopalladium(II) Complexes Containing Symmetrical Ligands

Ligand (L_2)	*trans* group	Chemical Shifts (ppm) Aromatic	Bridgehead	Pd-Me
pz_2CH_2	Me	8.03(H_5), 7.98(H_3), 6.38(H_4)	6.85	0.83
	I	8.21(H_5), 7.82(H_3), 6.57(H_4)		
pz_2CHMe	Me	8.21(H_5), 8.03($H_{3,5}$), 7.81(H_3)	7.28(q)	0.84
	I	6.56(H_4), 6.38(H_4)	2.59(d)	
pz_2CMe_2	Me	8.15(H_5), 7.90(H_3), 6.39(H_4)	2.79	0.85
	Cl	8.29(H_5), 7.78(H_3), 6.52(H_4)		
	Me	8.13(H_5), 8.00(H_3), 6.39(H_4)	2.72	0.84
	Br	8.29(H_5), 7.80(H_3), 6.54(H_4)		
	Me	8.14(H_5), 8.11(H_3), 6.37(H_4)	2.83	0.83
	I	8.30(H_5), 7.81(H_3), 6.55(H_4)		
mim_2CH_2	Me	7.52($H_{4(5)}$), 7.00($H_{5(4)}$)	4.31	0.60
	I	7.22($H_{4(5)}$), 6.99 ($H_{5(4)}$)		
mim_2CHMe	Me	7.49($H_{4(5)}$), 6.97($H_{5(4)}$)	4.80(q)	0.62
	I	7.19($H_{4(5)}$), 6.99($H_{5(4)}$)	1.82(d)	
$mim_2C{=}CH_2$	Me	7.56($H_{4(5)}$), 7.15($H_{5(4)}$)	6.33	0.60
	I	7.37($H_{4(5)}$), 7.08($H_{5(4)}$)		
py_2CH_2	Me	9.12(H_6), 7.90(4), 7.66(H_3), 7.35(H_5)	4.91	0.77
	I	8.61(H_6), 8.05(H_4), 7.81(H_3), 7.54(H_5)	4.61	
py_2CHMe	Me	two isomers present	4.86(q),2.59(d)	0.77
	I	See experimental (ch.6)	5.42(q),2.04(d)	0.78
py_2CMe_2	Me	9.44(H_6), 7.92(H_4), 7.76(H_3), 7.32(H_5)	3.01	0.79
	I	8.74(H_6), 8.05(H_4), 7.89(H_3), 7.51(H_5)	2.16	
$py_2C{=}CH_2$	Me	9.23(H_6), 8.02(H_4), 7.76(H_3), 7.45(H_5)	6.16	0.67
	I	8.67(H_6), 8.16(H_4), 7.85(H_3), 7.64(H_5)		
bipy	Me	9.13(H_6), 8.50(H_3), 8.23(H_4)) 7.80-7.72	-	0.86
	Cl	8.72(H_6), 8.56(H_3), 8.30(H_4)) H_5		
	Me	9.31(H_6), 8.51(H_3), 8.22(H_4), 7.74(H_5)	-	0.86
	Br	8.73(H_6), 8.58(H_3), 8.32(H_4), 7.81(H_5)		
	Me	9.53(H_6), 8.51(H_3), 8.20(H_4), 7.70(H_5)	-	0.83
	I	8.70(H_6), 8.58(H_3), 8.34(H_4), 7.85(H_5)		
phen	Me	9.77(H_2), 8.81(H_4), 8.06(H_3)) 8.25	-	1.00
	I	9.08 (H_9), 8.94(H_7), 8.19(H_8)) ($H_{5,6}$)		

The complexes {PdMeX(L_2)} (X=Cl, Br, I; L_2=bidentate N-donor ligands), except for {PdMeI(mim_2CHMe)} and {PdMeI(mimpyCHMe)}, exhibited variable temperature behaviour, and the results are readily interpreted in terms of rapid boat to boat ring inversion of the six membered chelate ring, as discussed for the analogous {$PdMe_2(L_2)$} complexes, figure 4.2.2-6. The complexes {PdMeI(mim_2CHMe)} and {PdMeI(pymimCHMe)}, on the other hand, displayed spectra which were consistent with the formation of one conformational isomer only, that with an axial methyl group, and hence an equatorial bridgehead proton.

Figure 4.2.2-6.



Assignment of the bridgehead protons in the low temperature limiting spectra of {PdMeI(L_2)} follows from the discussion in section 4.2.1, and the assignments are summarised in Table 4.2.2-4, and full assignments can be found in chapter 6.

The low temperature limiting spectra of {PdMeI(py_2CHMe)} and {$PdMe_2(py_2CHMe)$} are shown in figure 4.2.2-7, and they provide further evidence for conformational interpretations given earlier. The increased complexity of the former is due to the presence of inequivalent *trans* groups, and for {PdMeI(py_2CHMe)} isomer A has the bridgehead proton (CH) in an equatorial position and isomer B has this proton in an axial position, figure 4.2.2-7.

Previously it was proposed, for {$PdMe_2(py_2CHMe)$}, that with this assignment isomer B, containing an equatorial methyl group, would experience steric crowding between the equatorial methyl and the H_3 pyridine protons. To alleviate this crowding further puckering of the chelate ring occurs to place the bridgehead proton

closer to palladium compared with {$PdMe_2(py_2CH_2)$}, and thus a downfield shift is observed for this proton in the N.M.R. spectrum.

Table 4.2.2-4. Bridgehead Chemical Shifts for the low Temperature Limiting Spectra of {$PdMeX(L_2)$}

PdMeX(L_2) L2	X	Coalescence Temperature (K)	Chemical Shift (^nJ)
pz_2CH_2	I	275	7.01, d, CH_{eq} (^2J=14.4) 6.73, d, CH_{ax} (^2J=14.4)
pz_2CHMe	I	283 (CH)	A 7.37, q, CH_{eq} (^3J=6.7) 2.62, d, CMe_{ax} (^3J=6.7)
		278 (CMe)	B 7.30, q, CH_{ax} (^3J=6.8) 2.53, d, CMe_{eq} (^3J=6.8)
pz_2CMe_2	Cl	243	2.86, s, CMe_{ax} 2.66, s, CMe_{eq}
	Br	260	2.93, s, CMe_{ax} 2.69, s, CMe_{eq}
	I	265	2.95, s, CMe_{ax} 2.70, s, CMe_{eq}
mim_2CH_2	I	Unresolved to 203	
mim_2CHMe	I	Unresolved to 203	
py_2CH_2	I	307	4.92, s, CH_{eq} (^2J=13.7) 4.61, s, CH_{ax} (^2J=13.6)
py_2CHMe	I	Remains resolved to 323	A 4.86, q, CH_{eq} (^3J=7.3) 2.59, d ,CMe_{ax} (^3J=7.3) B 5.42, q, CH_{ax} (^3J=7.1) ~2.04, d ,CMe_{eq} (obs).
py_2CMe_2	I	remains resolved to 323	3.01, s ,CM_{ax} 2.16, s, CMe_{eq}

Examination of molecular models reveals that a second consequence of increased puckering of the chelate ring is to increase the distance between the iodo-group and the adjacent pyridine proton, H_6^B. This effect is reflected in the N.M.R. spectrum by the upfield shift (*ca.* 0.25 ppm) of H_6^B compared with H_6^A.

The low temperature limiting spectrum of {$PdMeI(pz_2CHMe)$}, figure 4.2.2-8, displays similar behaviour to that discussed above, although in this instance the H_3^A

and H_3^B protons are separated by only 0.15 ppm. The smaller shift compared with {PdMeI(py_2CHMe)} may reflect a lower degree of puckering of the chelate ring, and hence may imply reduced steric hindrance between the equatorial methyl group and the adjacent aromatic protons, in this case the H_5 pyrazole protons. This observation is consistent with the previous proposal (page 126)that steric hindrance between an equatorial methyl group and adjacent aromatic protons is greater for {PdMeI(py_2CHMe)} than {PdMeI(pz_2CHMe)}.

Figure 4.2.2-7. ^{1}H NMR of {PdMeR(py_2CHMe)} (R=Me, I) in Acetone-D6.

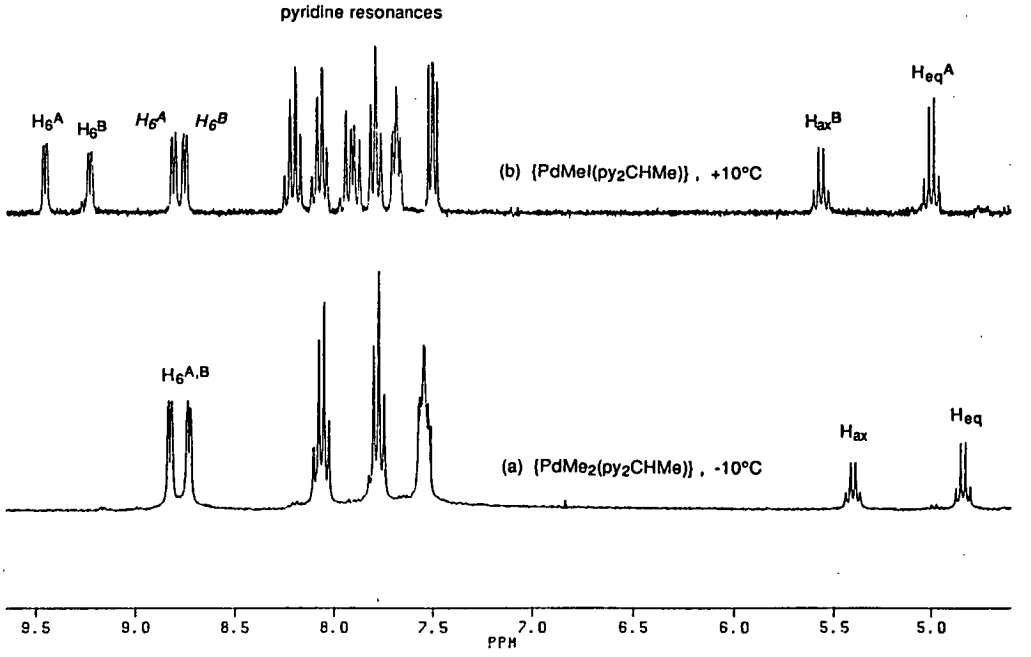
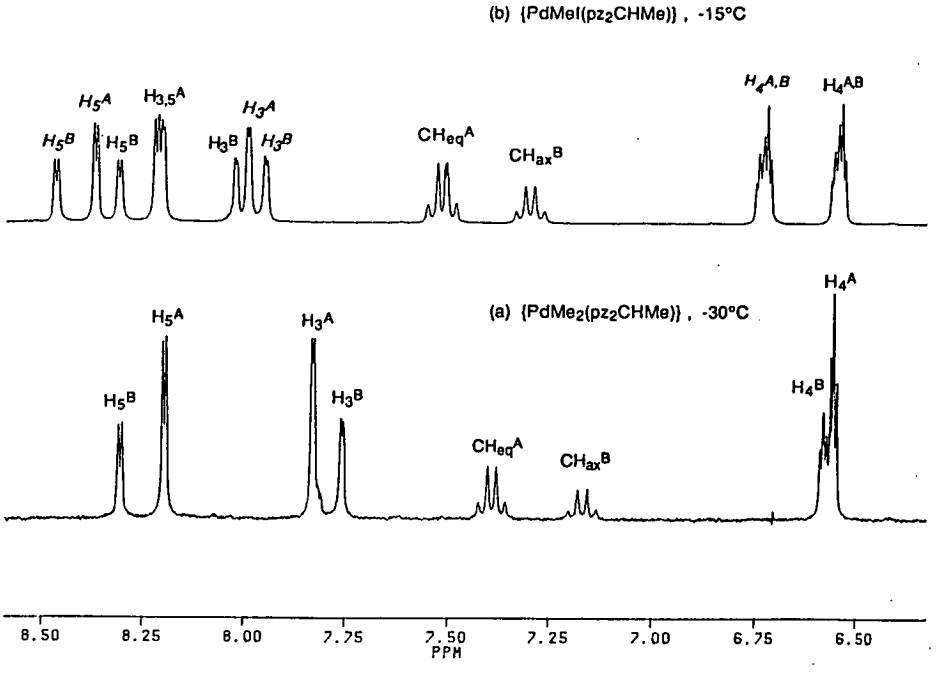


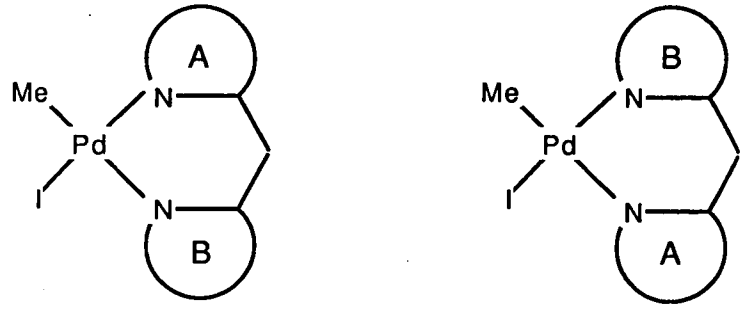
Figure 4.2.2-8. ^{1}H NMR of {PdMeR(pz_2CHMe)} (R=Me, I) in Acetone-D6.



(b) Unsymmetrical Ligands, R'RC

For monomethyliodopalladium(II) complexes containing unsymmetrical ligands, spectra similar to that discussed above are expected, but they will be further complicated by the ability of the complexes to adopt two isomeric structural forms. For example, in figure 4.2.2-9 heterocycle A can be *trans* to the iodo-group (I) or *trans* to the methyl group (II). The overall effect of this is to give a doubling-up of all resonances as (I) and (II) are chemically inequivalent.

Figure 4.2.2-9.



(I) (II)

While assignment of protons within each isomer is straightforward from a COSY spectrum, fortuitously all the complexes prepared displayed a preference for one isomer over the other, allowing proton assignments for each isomer directly from integration values. Further, assignment of *trans* groups follows from the discussion outlined previously, and in most cases is consistent with the position of the PdMe resonance (see Table 4.2.2-1).

For example, structural isomers for the complex {PdMeI(pzmimCH_2)} are depicted in figure 4.2.2-10, and the ambient temperature spectrum of the aromatic region for this complex is displayed in figure 4.2.2-11. Initial examination of this spectrum clearly illustrates the preference for one isomer over the other, and assignment of protons within each isomer follows readily; similar isomer ratios are obtained for the bridgehead and PdMe resonances.

Figure 4.2.2-10.

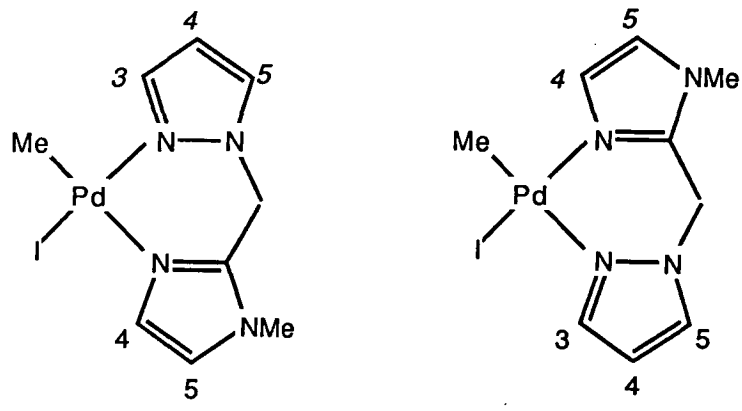
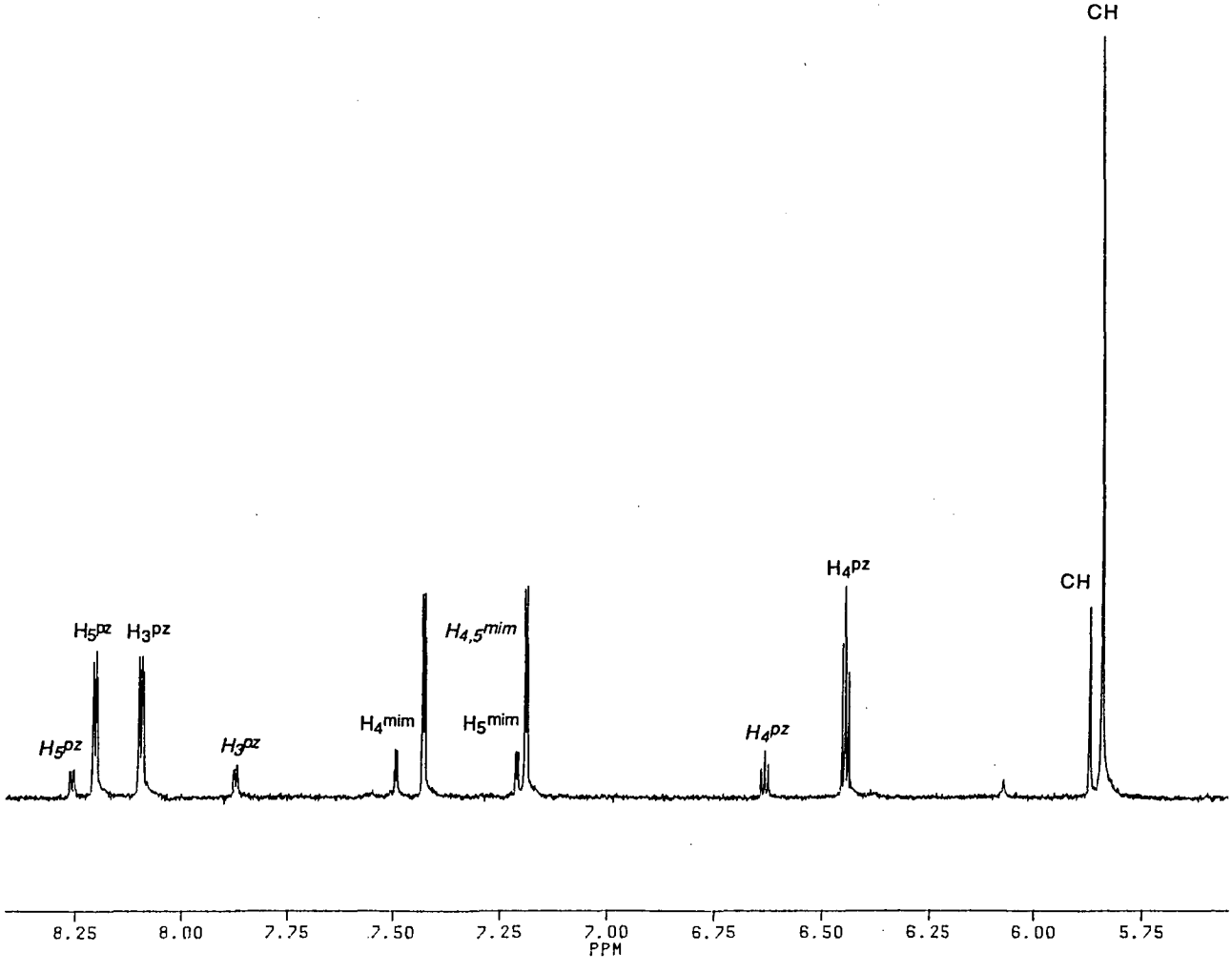


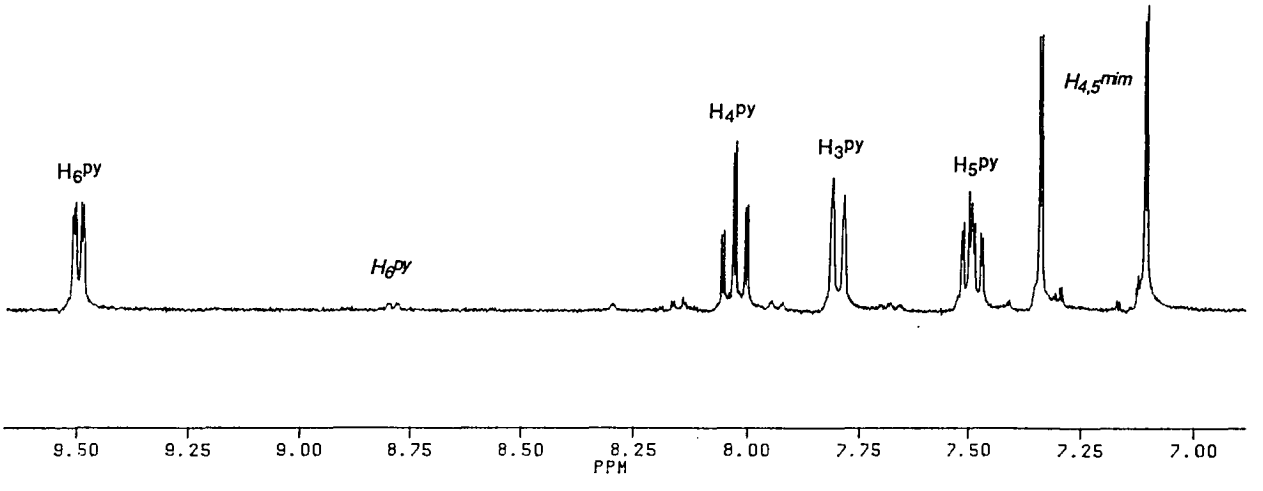
Figure 4.2.2-11. ^1H NMR of {PdMeI(pzmimCH_2)} in Acetone-D6.



Closer examination of the spectrum allows the assignment of the major isomer as (II), *i.e.* that isomer with pyrazole *trans* to methyl and *N*-methylimidazole *trans* to iodide, and thus the minor isomer is (I), figure 4.2.2-10. This assignment is based on the observation that H_3^{pz} is shifted downfield from H_3^{pz}, due to deshielding by the iodo-group. Further, the minor isomer, *i.e.* that with pyrazole *trans* to iodide, has the H_4^{pz} and H_5^{pz} resonances downfield from the analogous protons *trans* to methyl, as is indeed expected. Consistent with this interpretation the PdMe resonance of (I) (mim *trans* to methyl) is upfield of that for II (pz *trans* to methyl), as expected (see Table 4.2.2-1).

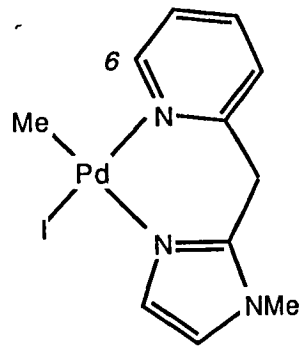
Similarly, reference to the ambient temperature spectrum for the complex {PdMeI(pymimCH$_2$)}, figure 4.2.2-12, illustrates that the major isomer present is that with the pyridine ring *trans* to methyl, *i.e.* II in figure 4.2.2-13. This is deduced from the downfield shift of the H_6^{py} proton, which is adjacent to the iodo-group, compared with H_6^{py} (at ~8.8 ppm), which is *trans* to the iodo-group.

Figure 4.2.2-12. ^{1}H NMR of {PdMeI(pymimCH$_2$)} in Acetone-D6.

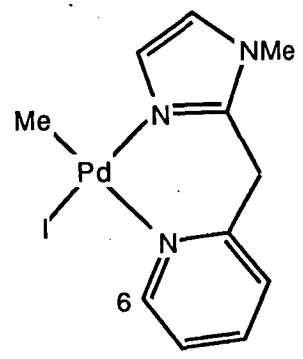


Using an approach analogous to that outlined above for {PdMeI(pzmimCH$_2$)} and (PdMeI(pymimCH$_2$)} spectral assignments for the other complexes prepared have been possible, and are reported for the major isomer only in Table 4.2.2-5. A full assignment may be found in chapter 6.

Figure 4.2.2-13.



(I)



(II)

Table 4.2.2-5. ^{1}H NMR Chemical Shifts for Monomethyliodopalladium(II) Complexes Containing Unsymmetrical Ligands

Ligand	Chemical Shifts δ (ppm) Aromatic	Bridgehead	Pd-Me
pypzCH$_2$	9.29(H$_6$), 8.00(H$_4$), 7.70(H$_3$), 7.50(H$_5$)	5.85	0.87
pz *trans* I	8.13(H$_5$), 7.70(H$_3$), 6.51(H$_4$)		
pzmimCH$_2$	8.06(H$_5$), 7.95(H$_3$), 6.30(H$_4$)	5.70	0.76
mim *trans* I	7.29(H$_{4(5)}$), 7.05(H$_{5(4)}$)		
pymimCH$_2$	9.35(H$_6$), 7.89(H$_4$), 7.66(H$_3$), 7.35(H$_5$)	4.50	0.80
mim *trans* I	7.20(H$_{4(5)}$), 6.96(H$_{5(4)}$)		
pymimCHMe	9.46(H$_6$), 7.89(H$_4$), 7.65(H$_3$), 7.34(H$_5$)	4.86(q)	0.80
mim *trans* I	~7.21(H$_{4(5)}$), 6.98(H$_{5(4)}$)	2.24(d)	
pymimC=O	9.69(H$_6$), 8.25(H$_{3,4}$), 7.73(H$_5$)	-	0.82
mim *trans* I	7.78(H$_{4(5)}$), 7.38(H$_{5(4)}$)		
pymimC=CH$_2$	9.45(H$_6$), 8.01(H$_4$), 7.82(H$_3$), 7.40(H$_5$)	6.42	0.77
mim *trans* I	~7.40(H$_{4(5)}$), 7.10(H$_{5(4)}$)	6.20	
pymim	9.31(H$_6$), 8.21(H$_3$), 8.14(H$_4$), 7.58(H$_5$)	-	0.91
mim *trans* I	7.56(H$_{4(5)}$), 7.21(H$_{5(4)}$)		

Previously, it was noted that the isolated {PdMeI(L_2)} complexes displayed a preference for one isomer, and this observation assisted with the interpretation of N.M.R. spectra. While it may be argued that this may reflect the preferential crystallisation of one isomer, and not a preference for *trans* groups by the heterocyclic ring, *in situ* preparations without subsequent isolation confirm the ratios obtained above, Table 4.2.2-6. For example, for isolated {PdMeI(pymimCH_2)}, isomer ratios of 94%:6% were obtained, compared with 94%:6% and 92%:8% for *in situ* preparations from {PdMe(m-I)(SMe_2)}$_2$ and {$PdMe_2$(pymimCH_2)}, respectively. This behaviour leads to the series py>pz>mim, which represents the decreasing preference for the heterocyclic ring to be *trans* to methyl.

Table 4.2.2-6. Isomeric Ratios Obtained for PdMeI(II) Complexes of Unsymmetrical Ligands

		In situ Preparation		
Ligand (L_2)	Isolated	{PdMe(μ-I)(SMe_2)}$_2$ + L_2	{$PdMe_2(L_2)$} + MeI	Assignment
pypzCH_2	80%	80%	80%	py *trans* Me
	(20%)	(20%)	(20%)	pz *trans* Me
pzmimCH_2	79%	81%	81%	pz *trans* Me
	(21%)	(19%)	(19%)	mim *trans* Me
pymimC=O	91%	~100%	91%	py *trans* Me
	(9%)	-	(9%)	mim *trans* Me
pymimC=CH_2	100%	93%	94%	py *trans* Me
	10%	(7%)	(6%)	mim *trans* Me

Finally, the methane linked complexes displayed variable temperature N.M.R. behaviour analogous to that described previously, and interpretation of these effects is identical to that discussed for the corresponding dimethylpalladium(II) complexes, see section 4.2.1.

4.3 METHYPALLADIUM(II) COMPLEXES CONTAINING TRIDENTATE LIGANDS

^{1}H N.M.R. spectra of the complexes {$PdMe_2(L_3)$} and {$PdMeI(L_3)$} (L_3=tridentate ligands) were recorded in acetone-D6. All of the complexes, except for {$PdMe_2(pymim_2CH)$}, displayed broad resonances at ambient temperature consistent with the presence of dynamic processes involving exchange of free and coordinated donor groups. Cooling, to slow the rate of exchange, gave spectra which display free and coordinated ring environments for those complexes exhibiting exchange at ambient temperature.

Assignment of free and bound donor rings in the low temperature limiting spectra is straightforward, for example, resonances for coordinated groups appear downfield from the free ligand values, and in a similar position to that for the corresponding bidentate complex, while protons for the un-coordinated ring resonate at a similar position to that observed for the free ligand.

At low temperature two conformational isomers for the complexes {$PdMeR(L_3)$} (R=Me,I) are possible, one containing an equatorial bridgehead proton, and the other an axial bridgehead proton. All of the tridentate ligand complexes displayed a preference the bridgehead proton in an equatorial orientation, presumably resulting from the greater steric interaction that would occur between an equatorial aromatic ring (un-coordinated) and the adjacent protons of coordinated pyridine or pyrazole, and the *N*-methyl protons of coordinated imidazole.

Further, the un-coordinated axial aromatic ring may be present in several orientations, *e.g.* 'parallel' to the metal square plane, and 'perpendicular' to the square plane. Differentiation between these is possible from the position of the PdMe resonance, compared with the analogous bidentate complexes, following essentially the technique developed by Canty and Marker[11] for solution structure determinations of $[MeHgL]^+$ cations. For example, with the axial group 'parallel' to the square plane shielding of the PdMe group occurs, and thus, compared with the corresponding bidentate complexes, an upfield shift of this resonance results. This effect is not

expected for the 'perpendicular' orientation, and the PdMe group is relatively unperturbed compared with the analogous bidentate complexes.

To facilitate discussion, both {$PdMeI(L_3)$} and {$PdMe_2(L_3)$} complexes are reported together under the general headings Symmetrical Ligands (pz_3CH and py_3CH) and Unsymmetrical Ligands (pz_2pyCH, pz_2mimCH, py_2mimCH and $pymim_2CH$). Full assignments are given, with rings *trans* to methyl denoted by plain text, while those *trans* to iodide are denoted by *italics* and un-coordinated groups are denoted by f (free).

4.3.1 Symmetrical Ligands

Spectra of {$PdMe_2(py_3CH)$}, together with the free ligand spectrum, are displayed in figure 4.3.1-1. At ambient temperature the complex displayed four broad resonances, and at -70°C displayed two ring environments in 2:1 ratio, as expected for a static system displaying coordinated and un-coordinated groups. This behaviour is consistent with facile exchange of coordinated and un-coordinated donor groups, figure 4.3.1-2.

Figure 4.3.1-1. Variable Temperature ^1H NMR of {$PdMe_2(py_3CH)$} in Acetone-D6.

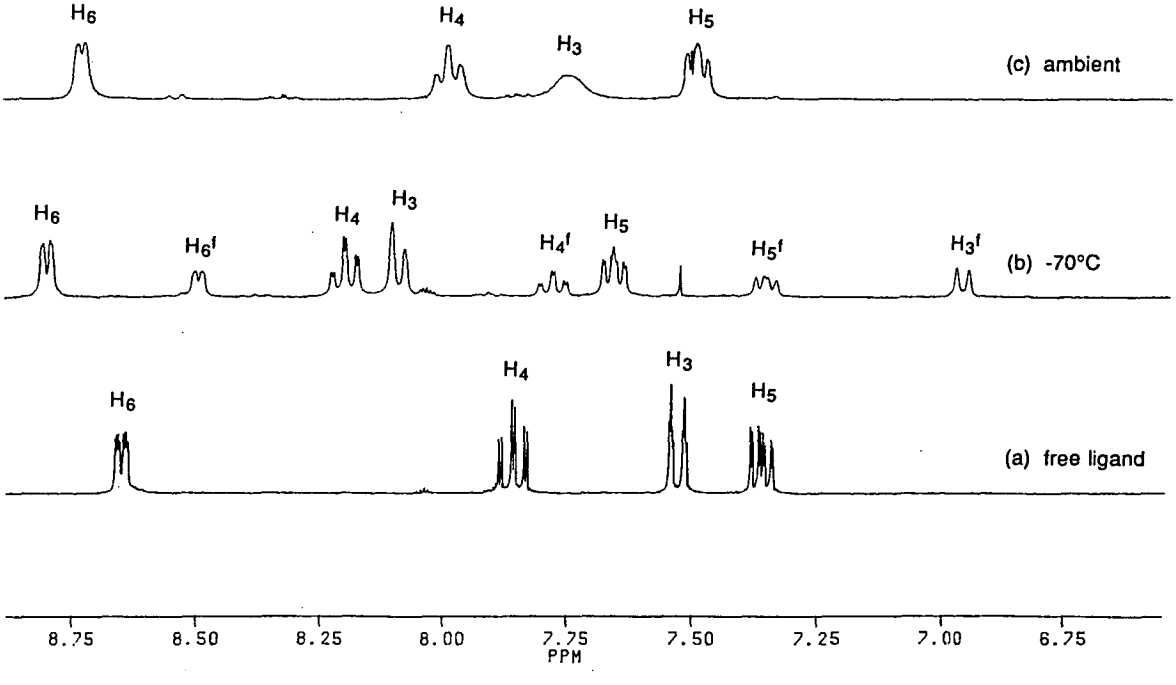
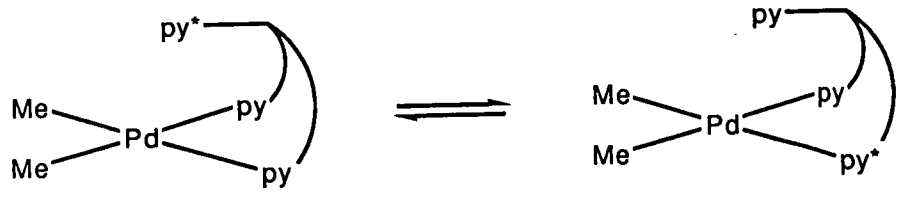
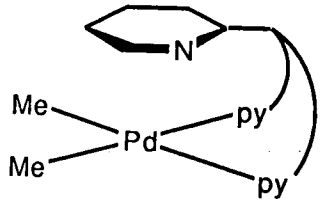


Figure 4.3.1-2.



Assignment of protons within each ring system follows directly from the integration values, and the proposed structure for the complex (figure 4.3.1-3) shows the un-coordinated pyridine ring in an axial position, 'parallel' to the metal square plane. This orientation of the ring is deduced from the observed upfield shift of *ca.* 0.40 ppm for the PdMe resonances in $\{PdMe_2(py_3CH)\}$ compared with these groups in the corresponding bidentate ligand complex $\{PdMe_2(py_2CH_2)\}$, and results from shielding by the axial pyridine ring. Consistent with this orientation is the upfield shift of the H_3 axial pyridine proton, which is shielded (compared to the free ligand) by the adjacent **coordinated** pyridine rings. The H_4 and H_6 protons also fall within the pyridine shielding cones and are thus shielded, although to a lesser extent than H_3; the H_5 proton, which is directed away from these cones appears unperturbed compared with the free ligand.

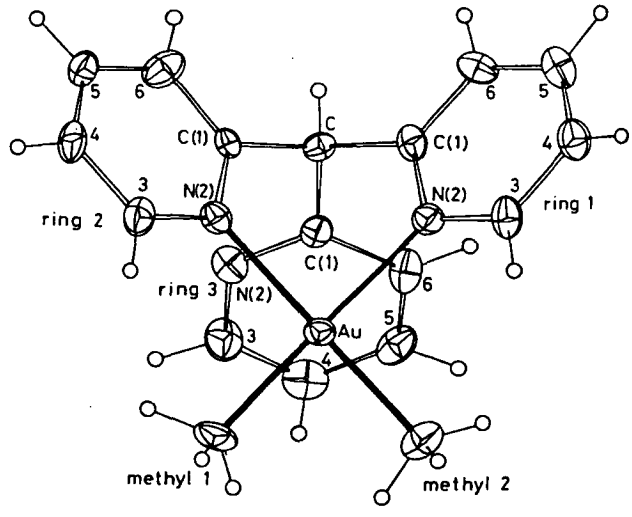
Figure 4.3.1-3.



A similar structure in the solution state has been proposed for the analogous dimethylgold(III) cation $[AuMe_2(py_3CH)]^+NO_3^-$.[12] The basis for this assignment was the upfield shift of 0.44 ppm for the Au-Me_2 resonances compared with this group in

$[AuMe_2(py_2CH_2)]^+NO_3^-$, and an X-ray structure determination revealed this orientation in the solid state, figure 4.3.1-4.

Figure 4.3.1-4.



Similar solution state behaviour was observed for $\{PdMe_2(pz_3CH)\}$, figure 4.3.1-5. The ambient temperature spectrum displayed three broad aromatic resonances, and at low temperature two pyrazole environments in *ca.* 2:1 ratio are seen. In this complex, however, the axial pyrazole group is perpendicular to the metal square plane, with the H_5^f pyrazole proton over palladium, figure 4.3.1-6. This assignment is based on the absence of shielding of the PdMe group, *i.e.* for $\{PdMe_2(pz_3CH)\}$ for PdMe groups resonate at 0.06 ppm while for $\{PdMe_2(py_2CH_2)\}$ they occur at 0.11 ppm, and the observed downfield shift of the H_5^f axial pyrazole proton compared with the free ligand (~0.90 ppm). The downfield shift is consistent with deshielding of H_5^f by the adjacent palladium centre, as noted for [Pd(2-(dimethylaminomethyl)phenyl-N(benzo[h]quinoline)]NO_3.[7]

An X-ray structure determination of $[AuMe_2(pz_3CH)]NO_3$ demonstrated a similar orientation for the axial group, except in this instance N(2) of the free pyrazole group was directed towards gold, and thus H_5^f directed away from the gold centre,[13] figure 4.3.1-7. For this complex a weak Au····N(2) axial interaction was proposed,[13]

and the preference exhibited by palladium may reflect a lower residual Lewis acidity for the palladium(II) kernel compared with the gold(III) kernel in the cation.

Figure 4.3.1-5. Variable Temperature ^1H NMR of $\{PdMe_2(pz_3CH)\}$ in Acetone-D6.

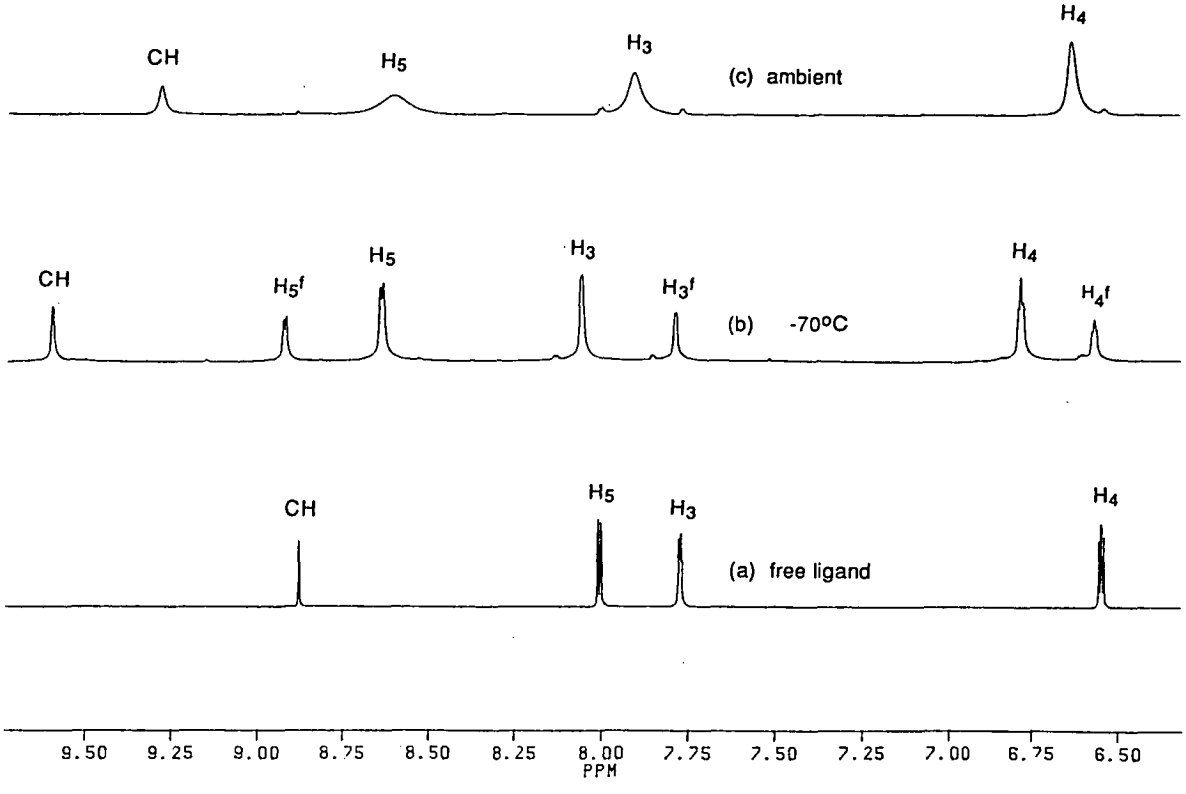
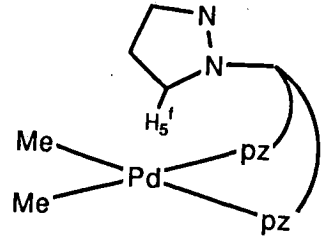
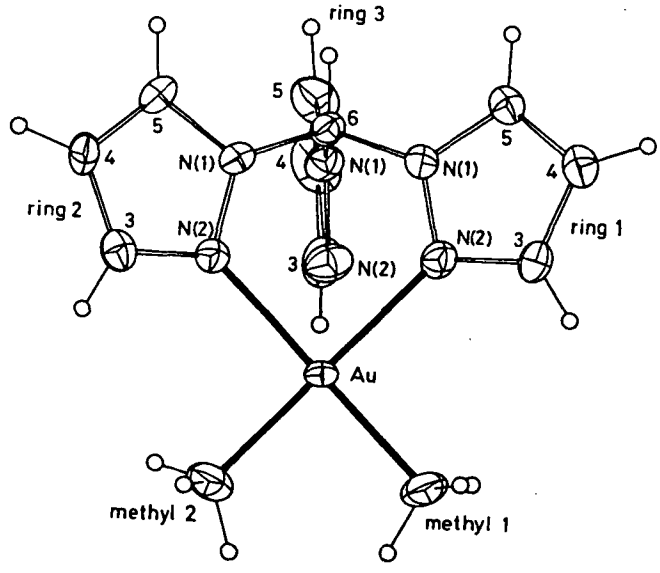


Figure 4.3.1-6.



Substitution of one of the methyl groups in $\{PdMe_2(L_3)\}$ by an iodo-group is expected to cause further complication of the low temperature spectra, as all groups will be inequivalent, *i.e.* bound groups are either *trans* to methyl or *trans* to iodide. Differentation of these groups is possible from the discussion outlined previously.

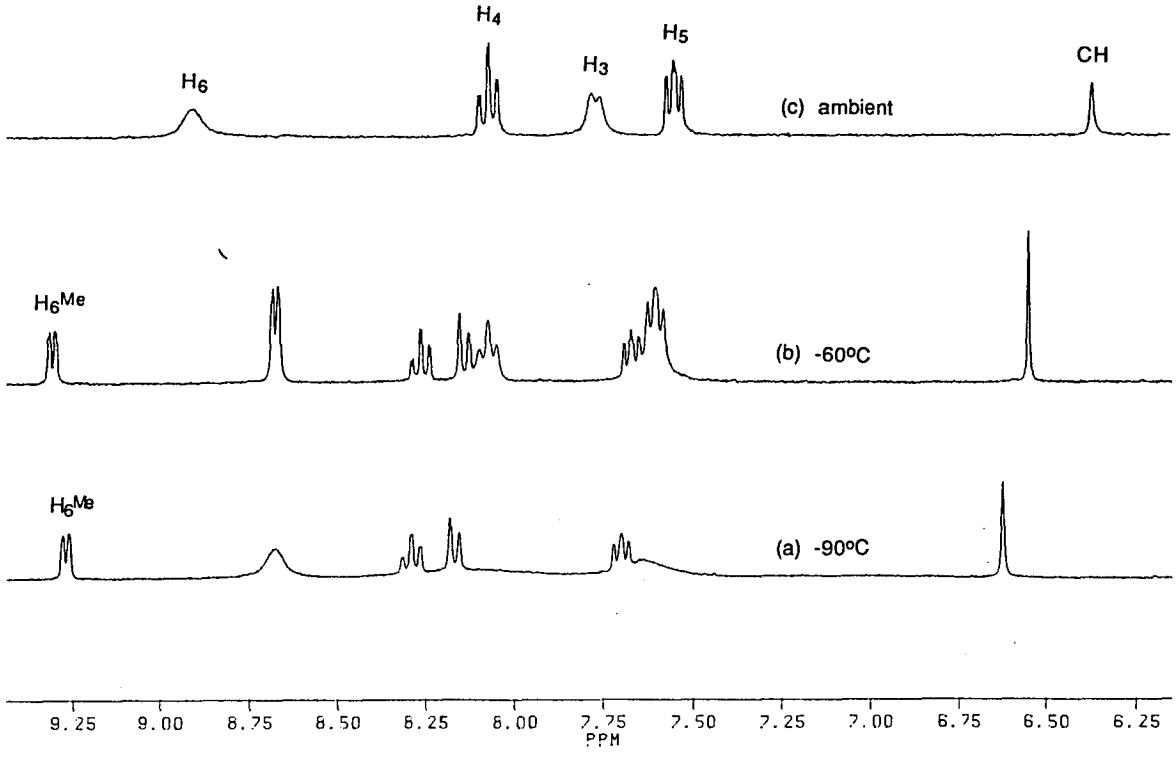
Figure 4.3.1-7.



The ambient temperature spectrum of the aromatic region of {PdMeI(py_3CH)} is displayed in figure 4.3.1-8c, and exhibits features similar to those observed for {$PdMe_2(py_3CH)$}. Cooling to -60°C gave a spectrum containing two pyridine environments in 2:1 ratio, and further cooling to -90°C resulted in resolution of the resonances attributed to the minor donor group, and broadening of all other aromatic resonances. This behaviour is consistent with different rates of exchange between the two coordinated sites and the un-coordinated site, so that the slower process, with rate K_1, is resolved (on the N.M.R. time scale) at a higher temperature than the other, scheme 4.3.1-1. The faster process with rate K_2, is unresolved at -90°C.

Assignment of the pyridine ring *trans* to methyl as the slowest exchanging group follows from the downfield position of the resolved H_6^{Me} resonance at -60°C, as it is deshielded by the adjacent iodo-group, and within 0.04 ppm of the analogous proton in {PdMeI(py_2CH_2)}. Although spectra for {PdMeI(py_3CH)} are not completely resolved at -90°C, the orientation adopted by the axial group may well be the same as that for {$PdMe_2(py_2CH_2)$}, with the ring 'parallel' to the metal square plane (figure 4.3.1-9).

Figure 4.3.1-8. Variable Temperature ^{1}H NMR of {PdMeI(py$_3$CH)} in Acetone-D6.



Scheme 4.3.1-1.

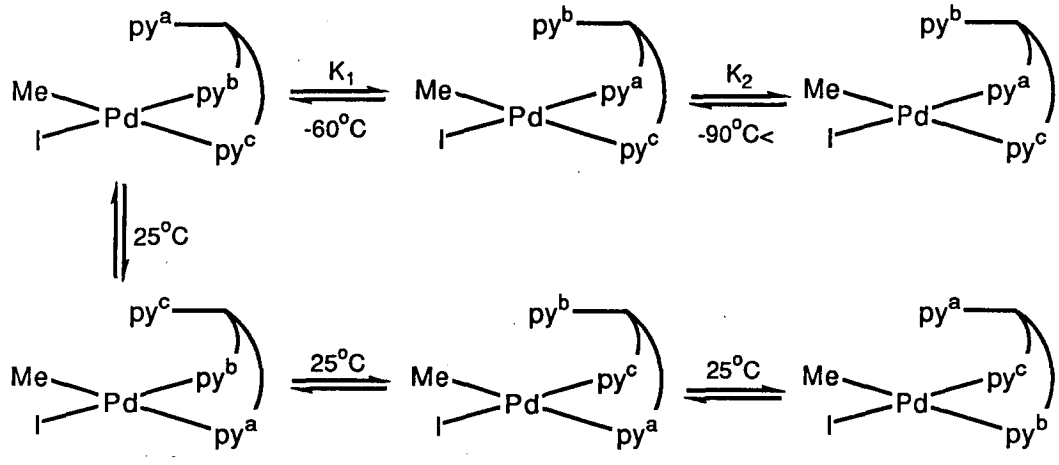
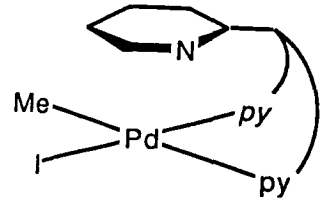


Figure 4.3.1-9.



The complex {PdMeI(pz_3CH)} displayed similar variable temperature behaviour to that found for {PdMeI(py_3CH)}, figure 4.3.1-10, but in this case the low temperature spectrum (figure 4.3.1-10b) exhibited nine aromatic resonances (although six of these are broad) representing 3 inequivalent pyrazole environments. Following the approach for {PdMeI(py_3CH)} the three sharp resonances have been assigned to the group *trans* to methyl.

Tentative proton assignments for the complex are given in figure 4.3.1-10, and based on the absence of shielding of the PdMe group, suggesting that the axial group is perpendicular to the metal plane, and the absence of deshielding of the H_5^f proton, suggesting the H_5^f proton is not adjacent to the palladium centre, the complex has been assigned the structure depicted in figure 4.3.1-11.

Figure 4.3.1-10.

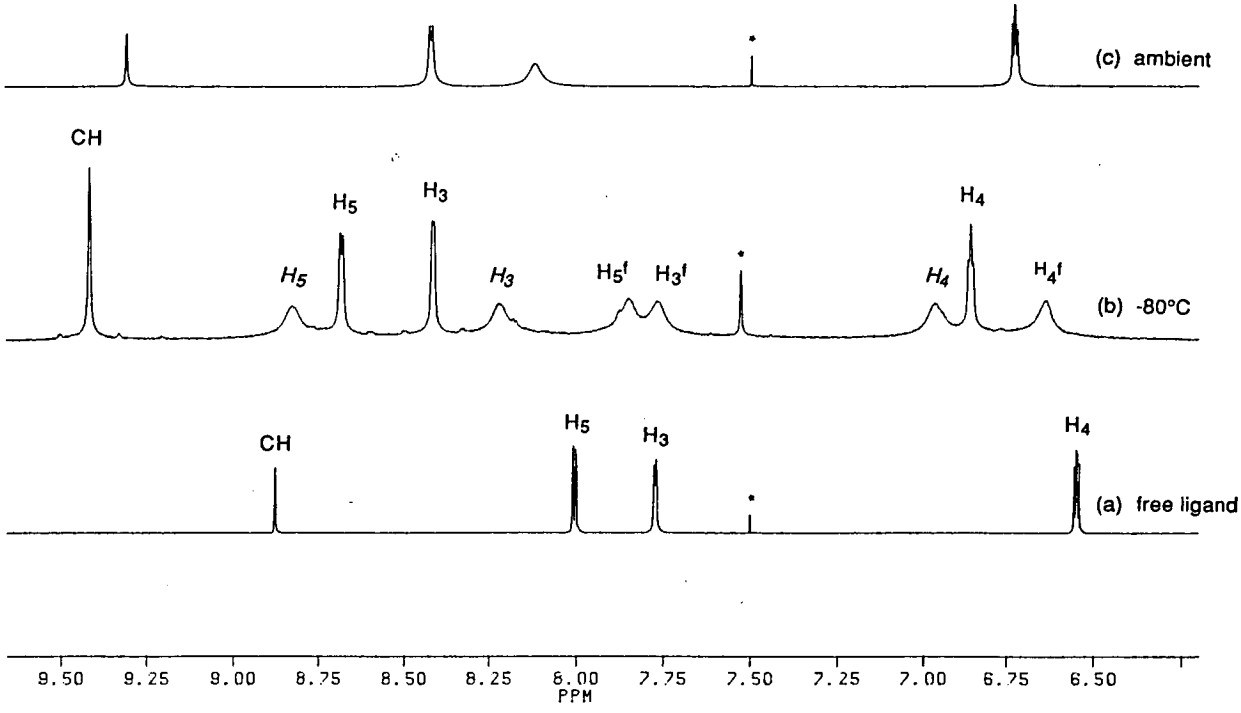
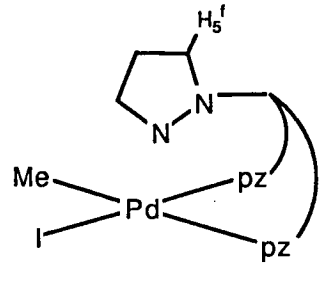


Figure 4.3.1-11.

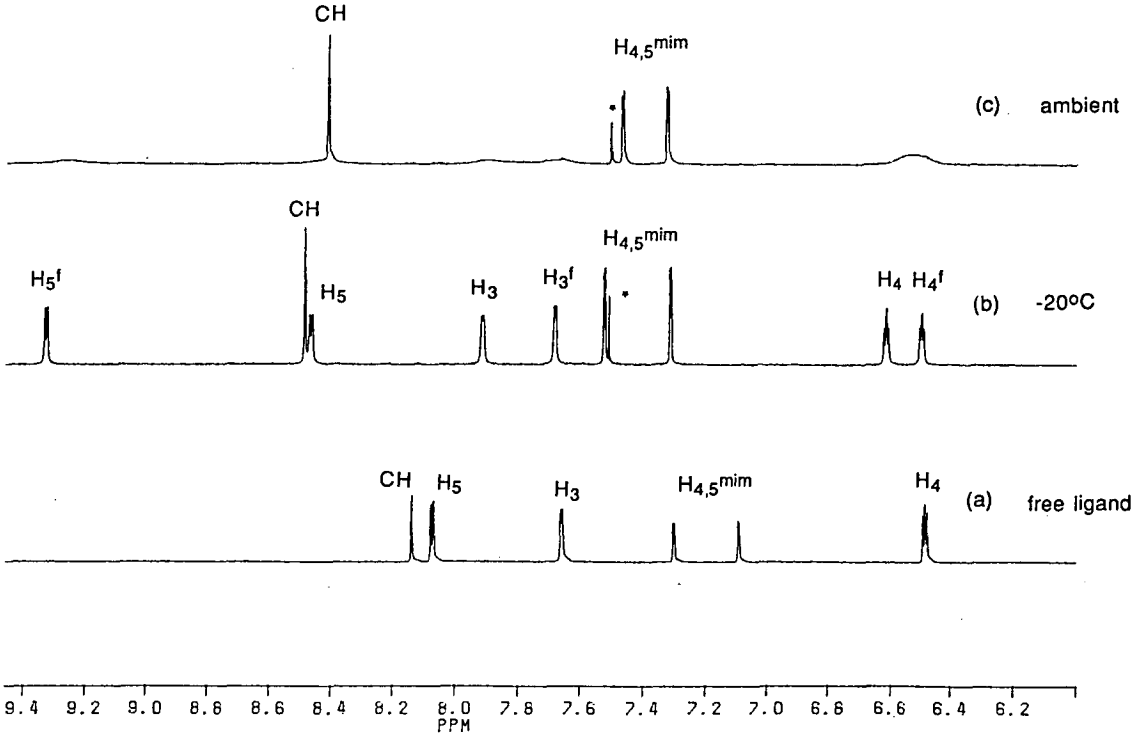


4.3.2 Unsymmetrical Ligands

(a) Ligands containing two pyrazole groups, pz_2RCH

Spectra of $\{PdMe_2(pz_2mimCH)\}$ are displayed in figure 4.3.2-1, and are readily interpreted in terms of exchange between coordinated and un-coordinated pyrazole donors, figure 4.3.2-2. The presence of two PdMe resonances, and the sharpness of the *N*-methylimidazole resonances, implies that this ring remains coordinated throughout the process. Cooling the solution to -20°C resulted in resolution of the pyrazole resonances, and from a COSY spectrum a full assignment is possible, figure 4.3.2-1b.

Figure 4.3.2-1. Variable Temperature ^1H NMR of $\{PdMe_2(pz_2mimCH)\}$ in Acetone-D6



The low temperature spectrum of $\{PdMe_2(pz_2mimCH)\}$ also exhibits two PdMe environments, as expected, and the position of these resonances is comparable to that found for the analogous complex $\{PdMe_2(pzmimCH_2)\}$, suggesting that the free pyrazole group is perpendicular to the metal plane. Further, the H_5^f proton is

shifted downfield by *ca.* 1.25 ppm from the free ligand position, while the H_4 and H_3 protons occur at similar positions to that found for the free ligand. This result suggests that the H_5^f proton is orientated over the palladium centre, and is consistent with the structure portrayed in figure 4.3.2-3.

Figure 4.3.2-2.

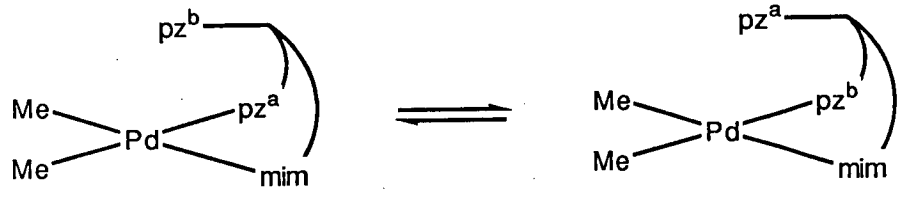
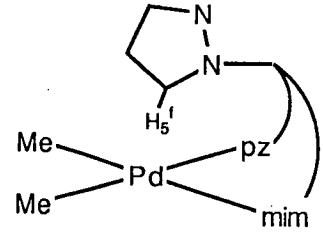


Figure 4.3.2-3.



The methyliodo-analogue {PdMeI(pz_2mimCH)} exhibits similar spectral behaviour, but at low temperature (-60°C) two isomers are observed, figure 4.3.2-4. Both isomers contain a bound pyrazole and a bound *N*-methylimidazole group, and display similar isomeric ratios and PdMe chemical shifts to that for the corresponding bidentate complex {PdMeI(pzmimCH_2)}. Thus, {PdMeI(pz_2mimCH)} has PdMe resonances at 0.76 (*trans* to pz) and 0.68 ppm (*trans* to mim) in a 1:7.3 ratio, while {PdMeI(pzmimCH_2)} has these groups at 0.76 (*trans* to pz) and 0.66 ppm (*trans* to mim) in a 1:3.8 ratio.

The major isomer at low temperature is denoted A in figure 4.3.2-5. This assignment is based on the downfield shift of the H_3 proton, which is adjacent to the iodo group, and the relative position of the PdMe resonances, *i.e.* PdMe *trans* to pyrazole is downfield from PdMe *trans* to *N*-methylimidazole, as expected (see section

4.2.2). Consistent with this assignment, the H_4 and H_4^f resonances are upfield from *H_4* which is *trans* to the iodo-group. The orientation of the axial pyrazole ring is discerned from the absence of shielding of the PdMe groups, and the deshielding observed for the H_5^f proton. A similar orientation of the axial group is present for the minor isomer (B), and this assignment is based on the observed deshielding of the H_5^f proton.

Figure 4.3.2-4. Variable Temperature ^1H NMR of {PdMeI(pz_2mimCH)} in Acetone-D6

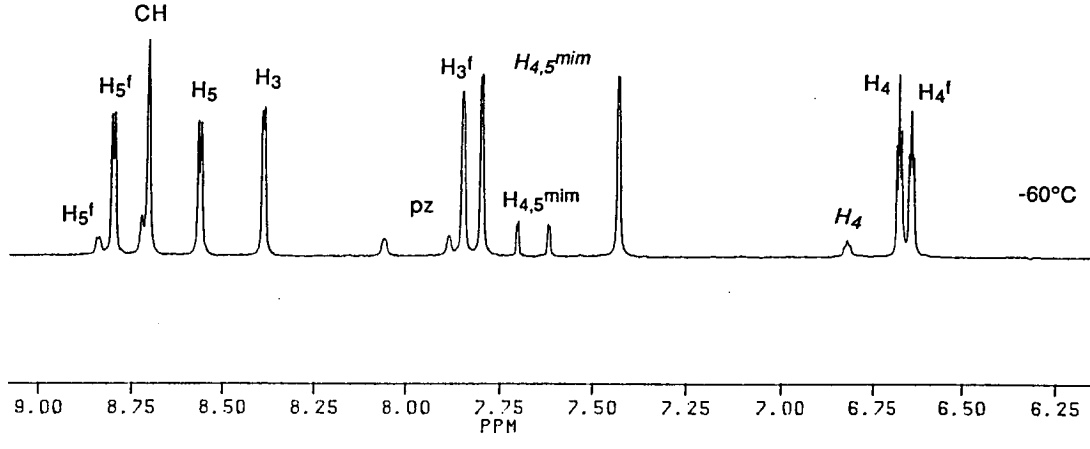
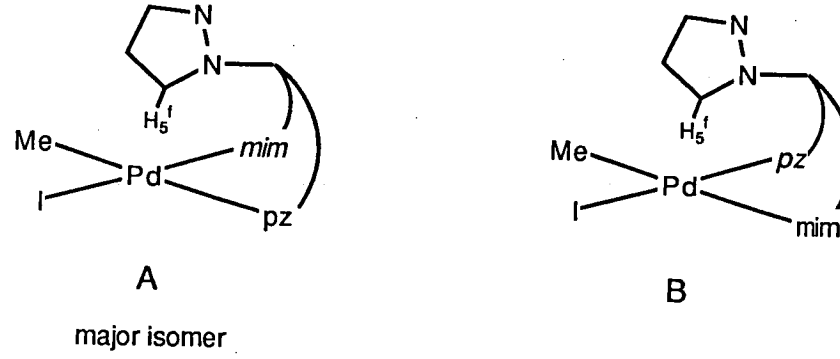


Figure 4.3.2-5.



The complex {$PdMe_2(pz_2pyCH)$} also exhibited temperature dependent N.M.R. spectra, figure 4.3.2-6, and at low temperature (-80°C) gave a spectrum displaying the presence of two isomers, A and B in figure 4.3.2-7. Resonances for

each of these isomers are readily differentiated from their integration values (A:B ~3:1), and with the aid of a COSY spectrum full assignment of the aromatic region has been possible (see chapter 6). Figure 4.3.2-8 displays an expansion of this region, and for clarity only those resonances arising from the major isomer together with important resonances for the minor isomer (denoted by (B)) are given.

Figure 4.3.2-6. Variable Temperature ^{1}H NMR of {$PdMe_2(pz_2pyCH)$} in Acetone-D6

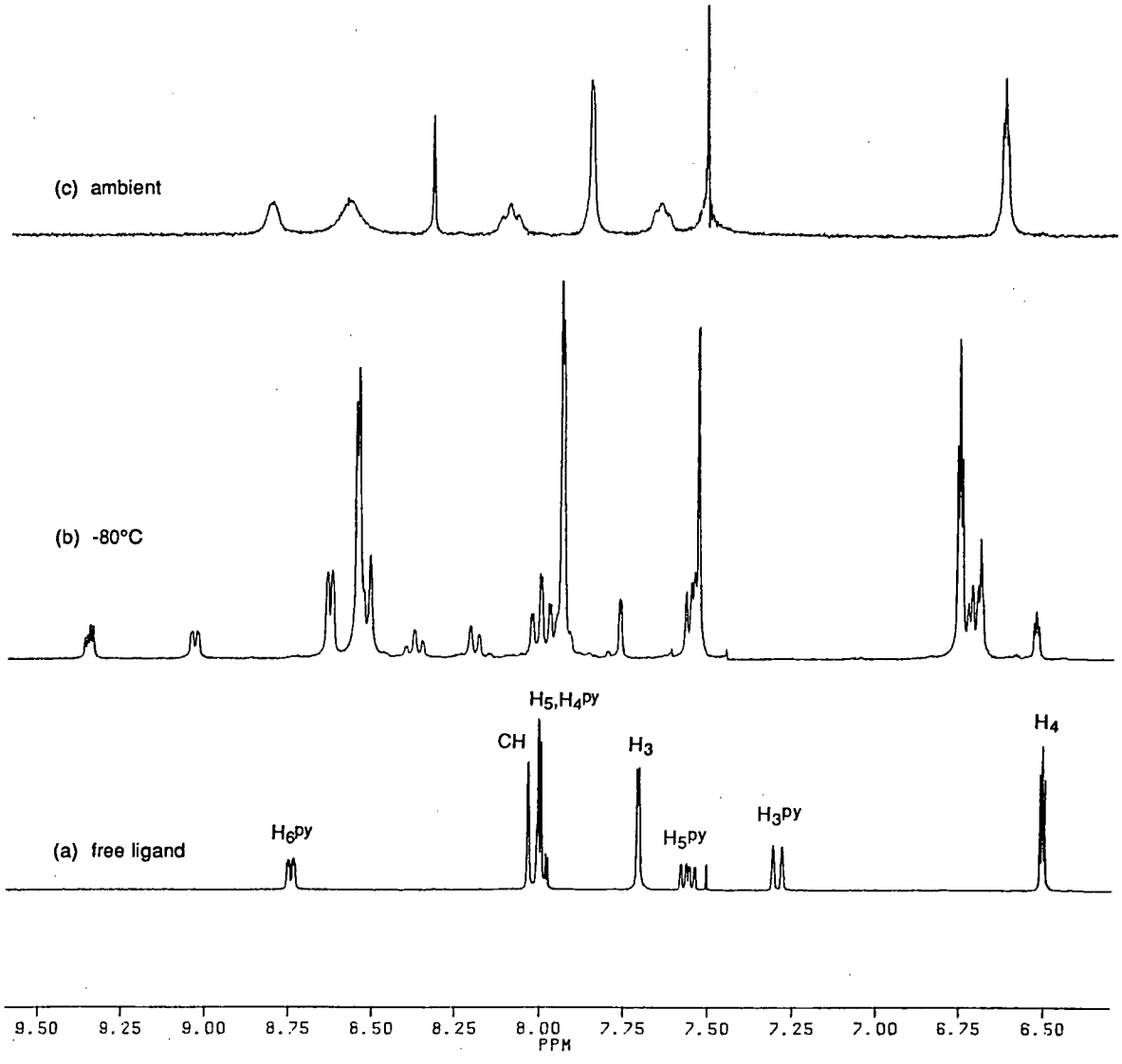


Figure 4.3.2-7.

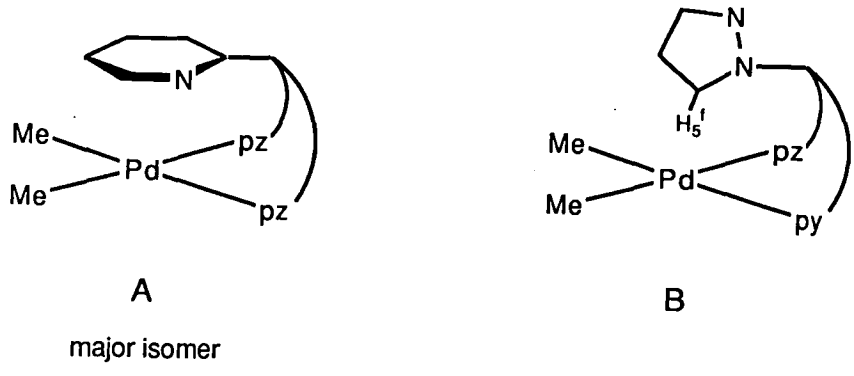
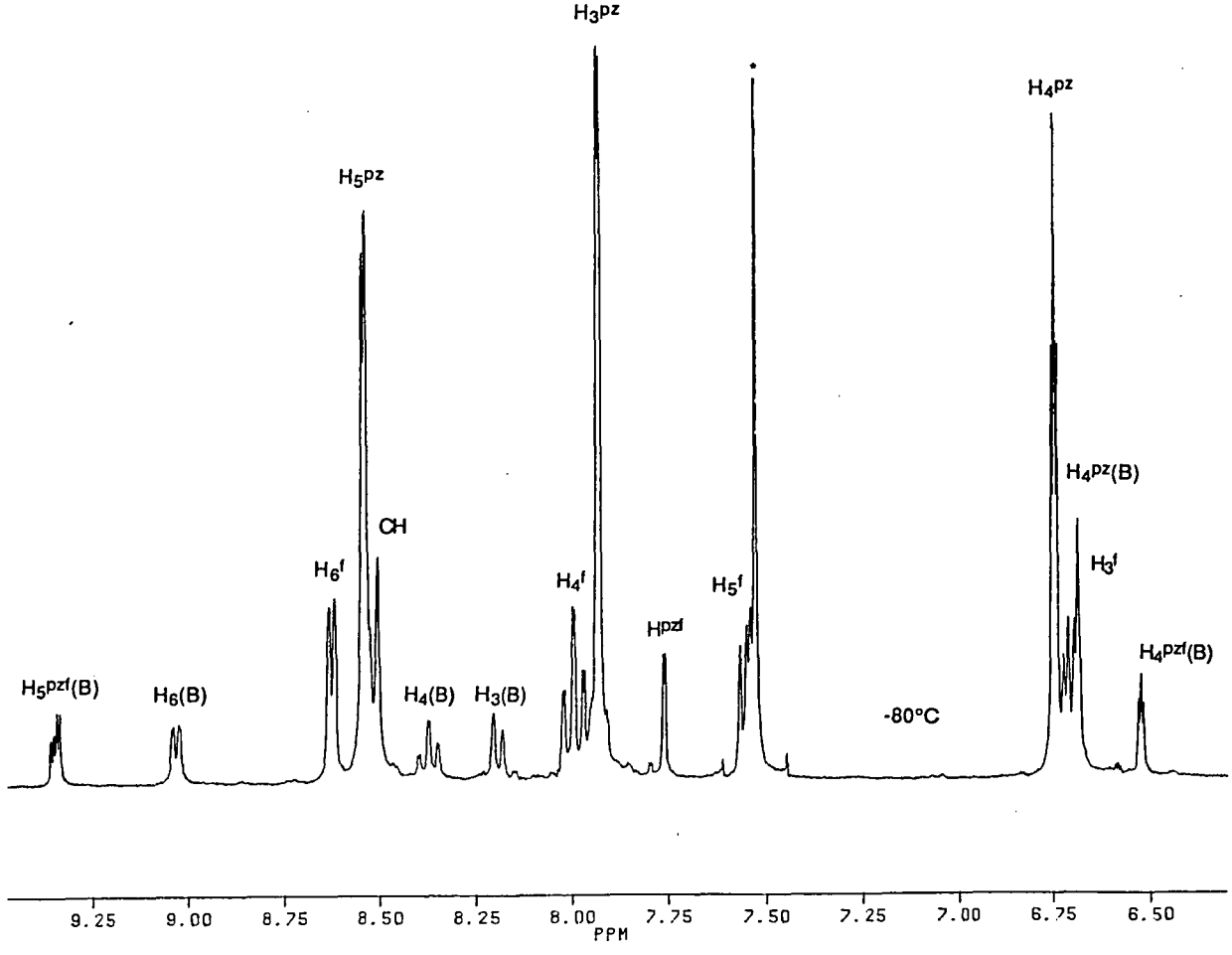


Figure4.3.2-8. ^1H NMR of {$PdMe_2(pz_2pyCH)$} in Acetone-D6 at -80°C



Assignment of A as the major isomer present at low temperature follows from the existence of only one PdMe resonance (at -0.2 ppm) of appropriate integration value and, consistent with this interpretation, two PdMe environments in 1:1 ratio for isomer B (at ~+0.1 ppm) are present.

The orientation of the free pyridine ring in isomer A, 'parallel' to the metal square plane is indicated by the observed shielding of the PdMe groups in $\{PdMe_2(pz_2pyCH)\}$ compared with those in $\{PdMe_2(pz_2CH_2)\}$, *i.e.* for the former they occur at -0.16 ppm, while for the latter they occur at +0.11 ppm. Consistent with this interpretation is the upfield shift, compared with the free ligand, of the H_3^f and, to a lesser extent, the H_4^f and H_6^f protons, figure 4.3.2-6 a, b. This shift results from the placement of these protons within the shielding cones of the adjacent pyrazole rings.

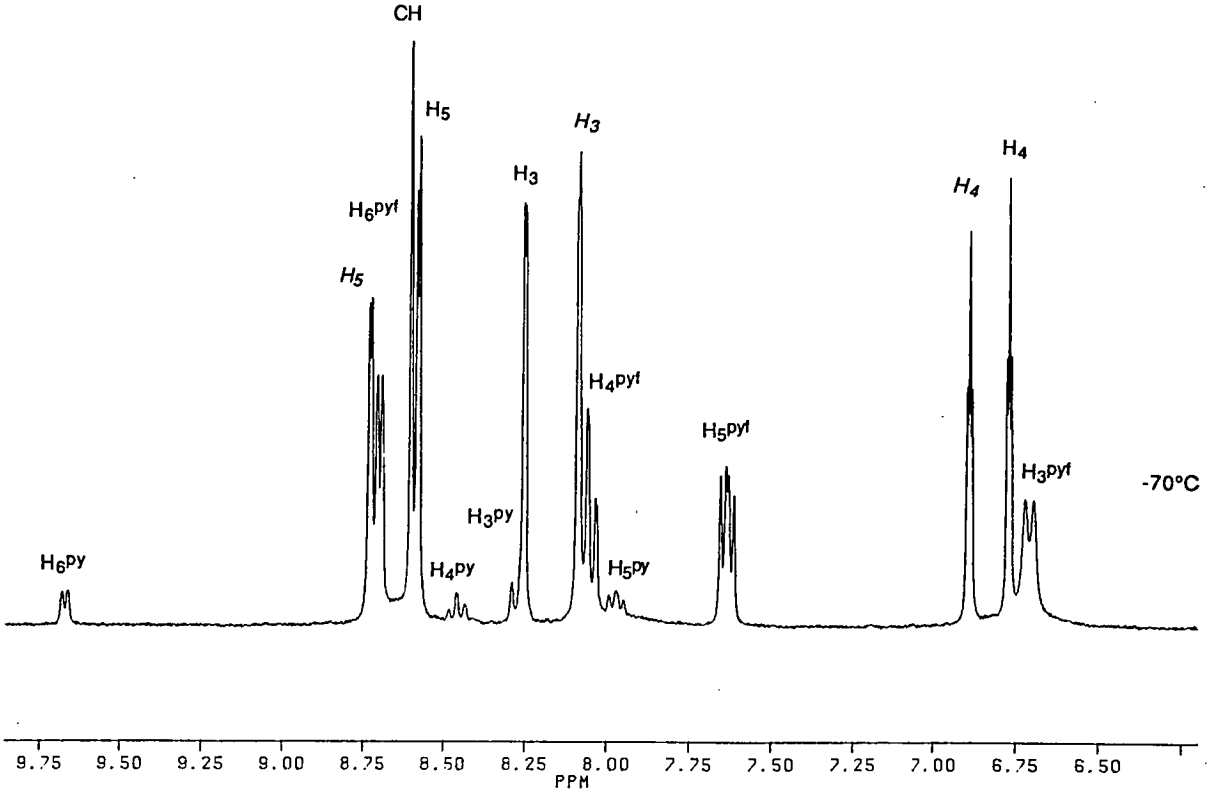
Similarly, the orientation of the axial pyrazole group in isomer B is deduced from the PdMe positions in $\{PdMe_2(pz_2pyCH)\}$ compared with those in the bidentate ligand analogue $\{PdMe_2(pypzCH_2)\}$, and the downfield shift observed for H_5^{pzf}(B) suggests this proton is adjacent to the palladium centre, figure 4.3.2-8. However, this resonance appears as a very close pair of doublets in *ca.* 2:3 ratio, with total integration value as expected.

An explanation for this behaviour must be consistent with the earlier deduction that H_5^{pzf} is close to the palladium centre, as other axial and equatorial orientations will give a resonance position for H_5^{pzf} comparable to, or upfield from, that found for the free ligand. The most likely explanation is that the H_5^{pzf} proton does not lie **directly** above the palladium centre but is positioned either side of the palladium atom, and due to the presence of different donor groups in the square plane these environments are inequivalent, giving two H_5^{pzf} resonances. A further consequence of the inequivalence of both 'sides' of the molecule is that a particular orientation is preferred, reflected in the 2:3 ratio observed for H_5^{pzf}, although assignment of which orientation is preferred is not possible. The placement of H_5^{pzf} directly over the palladium centre, perhaps forming an agostic interaction, appears unlikely as H_5^{pzf} in this orientation is expected to occur much further downfield than this proton in either of the 'off centred'

orientations proposed above. Further support for this interpretation is given in part (b) below.

The low temperature spectrum of {PdMeI(pz_2pyCH)} is displayed in figure 4.3.2-9, and, as was observed above for {$PdMe_2$(pz_2pyCH)}, preference for the isomer containing bound pyrazole groups is displayed. With the aid of a COSY spectrum, assignments for this isomer have been possible and are shown in figure 4.3.2-9. The structure for this complex is portrayed in figure 4.3.2-10A with the orientation of the axial pyridine ring deduced from the shielding of the PdMe groups in {PdMeI(pz_2pyCH)} compared with {PdMeI{pz_2CH_2)}, and the upfield shift of the H_3^{pyf} proton, shielded by the adjacent pyrazole rings.

Figure 4.3.2-9. ^{1}H NMR of {PdMeI(pz_2pyCH)} in Acetone-D6 at -70°C.



The minor isomer has been assigned the structure depicted in figure 4.3.2-10B. This assignment is based on the downfield shift observed for the H_6^{py} proton which is deshielded by the adjacent iodo-group. The orientation of the axial pyrazole ring is deduced from the observed upfield shift of the PdMe resonance compared with the

'bidentate' analogue {PdMeI(pypzCH$_2$)}, and the absence of a deshielded H$_5$[f] proton resonance between 8.8-9.5 ppm, implying that the axial ring is not perpendicular to the metal plane with H$_5$ adjacent to the palladium centre.

Figure 4.3.2-10.

A

major isomer

B

(b) Ligands containing pyridine and *N*-methylimidazole groups, pymim$_2$CH and py$_2$mimCH.

For {PdMe$_2$(py$_2$mimCH)} the sharpness of the *N*-methylimidazole protons (H$_{4(5)}$, H$_{5(4)}$) at both ambient (figure 4.3.2-11) and low temperature, together with the broadness of the PdMe resonances at ambient temperature, suggests that throughout the exchange process the *N*-methylimidazole group remains **coordinated**, but at higher temperatures readily undergoes site exchange between coordinated sites, figure 4.3.2-12, presumably *via* a five coordinate intermediate.

Figure 4.3.2-11. ^{1}H NMR of {PdMe$_2$(py$_2$mimCH)} in Acetone-D6.

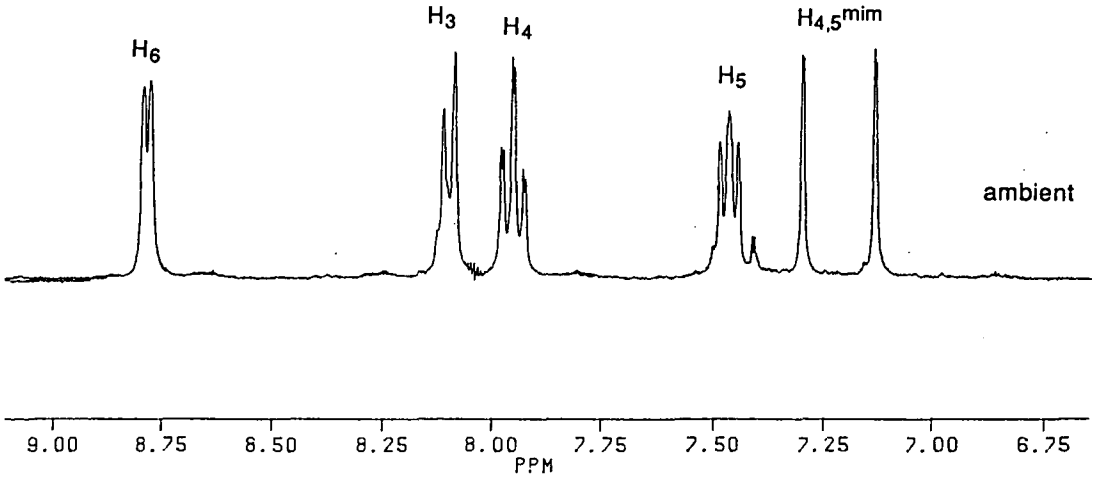
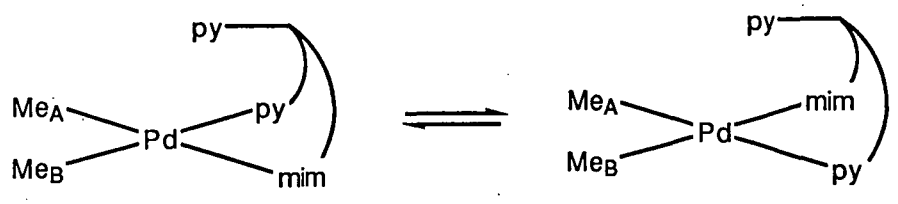


Figure 4.3.2-12.



The low temperature spectrum of {$PdMe_2(py_2mimCH)$} displays the behaviour anticipated, *i.e.* the spectrum exhibits a coordinated pyridine and *N*-methylimidazole group and an un-coordinated pyridine group. With the aid of a COSY spectrum, figure 4.3.2-13, full assignment of this spectrum has been possible, and assignments are displayed in figure 4.3.2-14.

Figure 4.3.2-13. COSY of {$PdMe_2(py_2mimCH)$} in Acetone-D6 at -70°C.

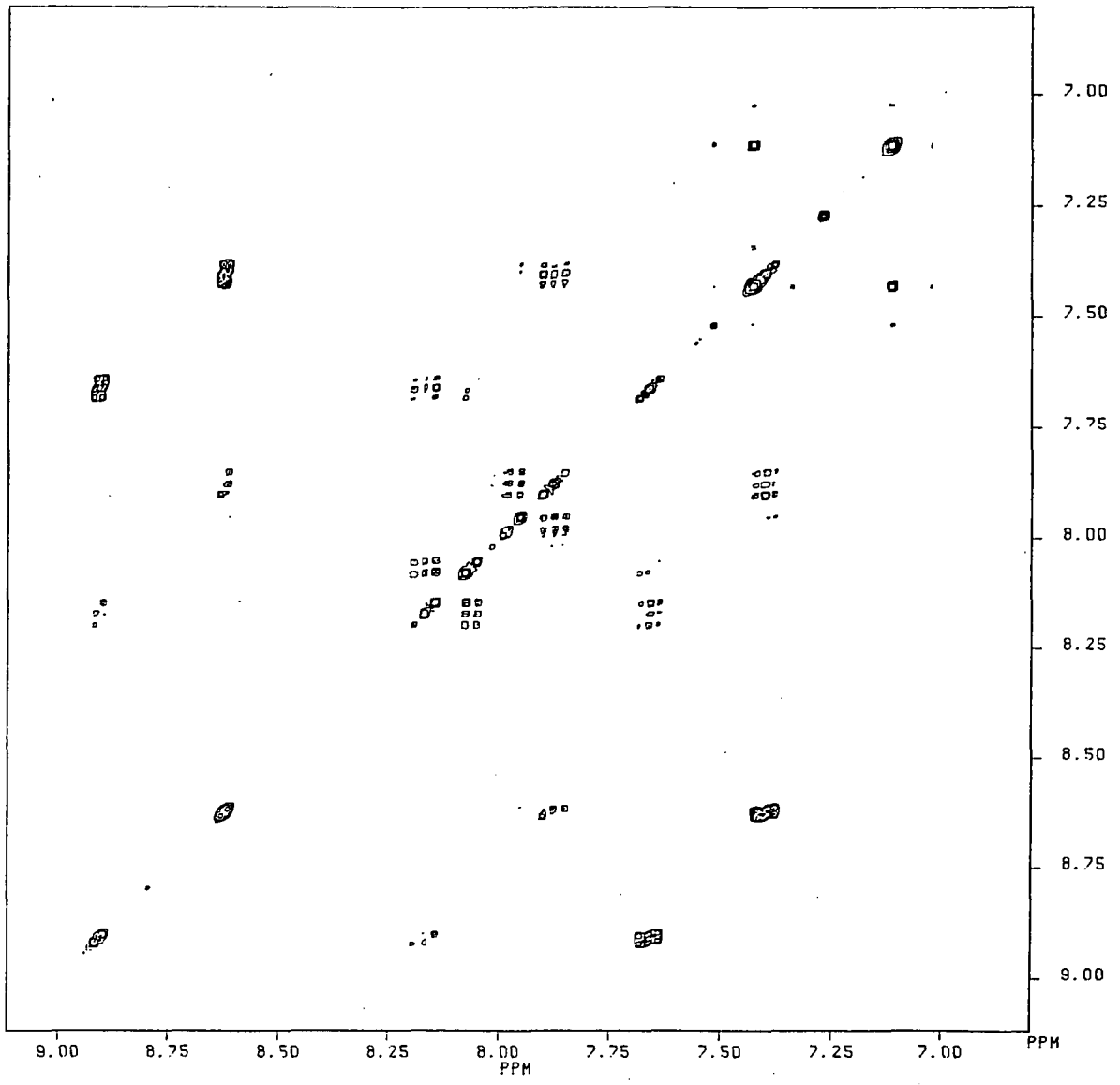
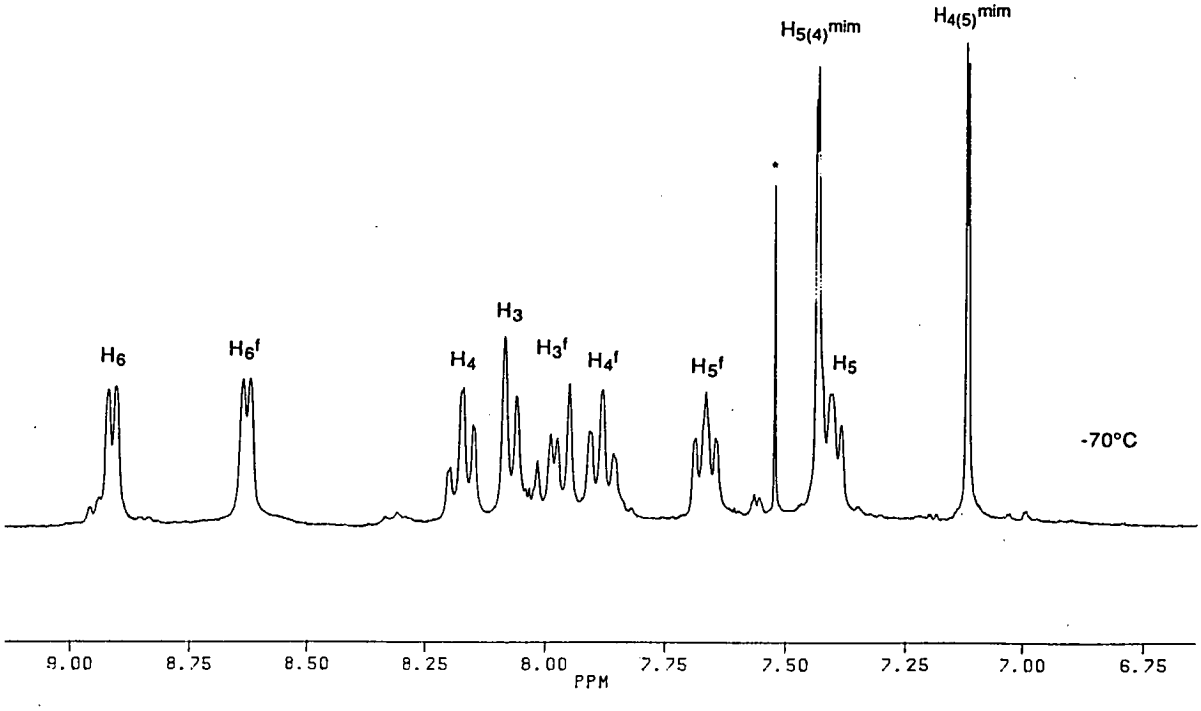


Figure 4.3.2-14. ^{1}H NMR of {$PdMe_2(py_2mimCH)$} in Acetone-D6 at -70°C.



The spectrum does, however, display one curious feature. The H_3^f proton appears as a multiplet, possibly a pair of doublets, instead of the expected doublet, and appears *ca.* 0.5 ppm downfield from H_3 in the free ligand. This behaviour suggests that the un-coordinated ring is positioned in an axial orientation perpendicular to the metal square plane, and with the H_3 proton adjacent to the palladium centre, figure 4.3.2-15. The appearance of the H_3^f proton as a pair of doublets indicates that H_3^f does not lie directly above the palladium centre but lies either side of the palladium atom, and this is supported by the observed 'splitting' of the PdMe resonances at low temperature, figure 4.3.2-16.

Figure 4.3.2-15.

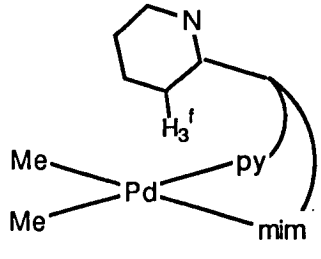
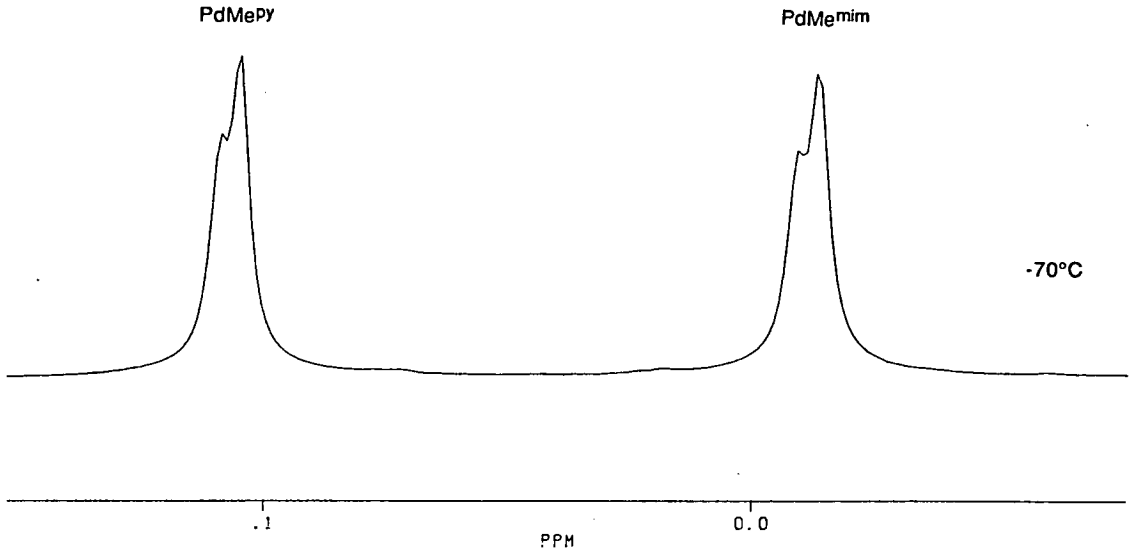


Figure 4.3.2-16. ^{1}H NMR of {$PdMe_2(py_2mimCH)$} in Acetone-D6 at -70°C.



The low temperature spectrum of the methyliodo-analogue {$PdMeI(py_2mimCH)$} is straightforward, figure 4.3.2-17, displaying only one conformation at low temperature, figure 4.3.2-18A. This assignment is based upon the presence of two pyridine environments, one *trans* to methyl, and the other in an axial position parallel to the metal square plane. These assignments are based on the downfield shift of the H_6 proton, which is adjacent to the iodo-group, and the observed shielding of the $H_3{}^f$ proton and the PdMe group.

Figure 4.3.2-17. ^{1}H NMR of {$PdMeI(py_2mimCH)$} in Acetone-D6 at -85°C.

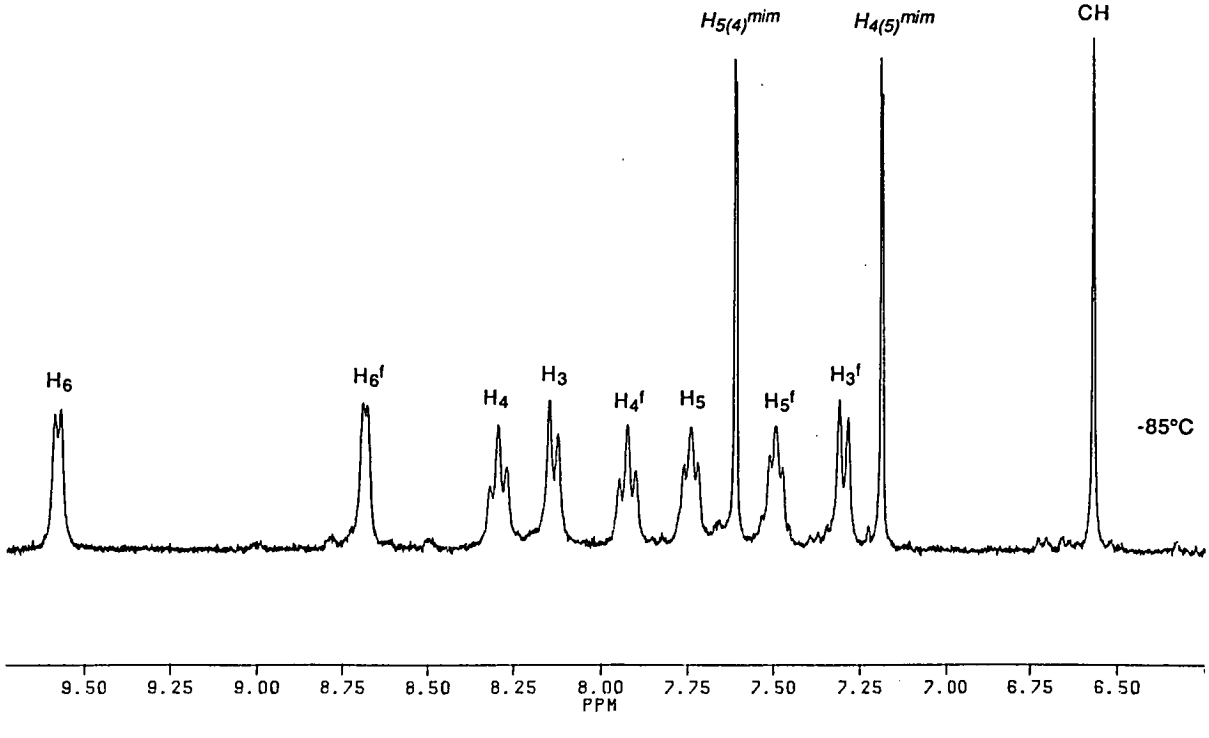
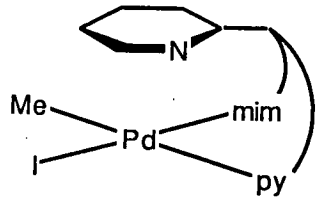
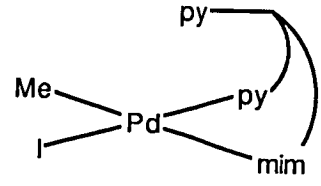


Figure 4.3.2-18.



A



B

Further, the presence of isomer A in preference to B is consistent with that found earlier for the bidentate complexes {PdMeI(pymimCRR')}, *i.e.* for mixed pyridine/*N*-methylimidazole ligands a striking preference (>90%) for pyridine groups to be *trans* to methyl upon complexation to palladium was observed.

The complex {$PdMe_2(pymim_2CH)$} displayed a very simple spectrum at ambient temperature, figure 4.3.2-19, which did not change upon warming to +45°C or cooling to -30°C. This complex has been assigned the structure depicted in figure 4.3.2-20, deduced from the presence of one *N*-methylimidazole environment, and the observed deshielding of the H_3^{pyf} proton, and is thus adjacent to the palladium centre. Consistent with the axial pyridine ring orientated perpendicular to the metal square plane, the PdMe resonance is at a similar position to that found for the bidentate ligand analogue.

While {$PdMe_2(pymim_2CH)$} appears to be static at ambient temperature, it is possible that the complex undergoes rapid site exchange of the *N*-methylimidazole groups. Indeed, this behaviour is suggested by the ambient temperature spectrum of the analogous complex {$PdMeI(pymim_2CH)$}. In this spectrum, resonances for both *N*-methylimidazole groups appear broad, figure 4.3.2-21b, while those for the pyridine and the PdMe moieties are sharp and well defined. Cooling this solution resulted in resolution of the *N*-methylimidazole resonances, but no change in the PdMe or pyridine resonances, figure 4.3.2-21a.

Figure 4.3.2-19. ^{1}H NMR of {$PdMe_2(pymim_2)$} in Acetone-D6.

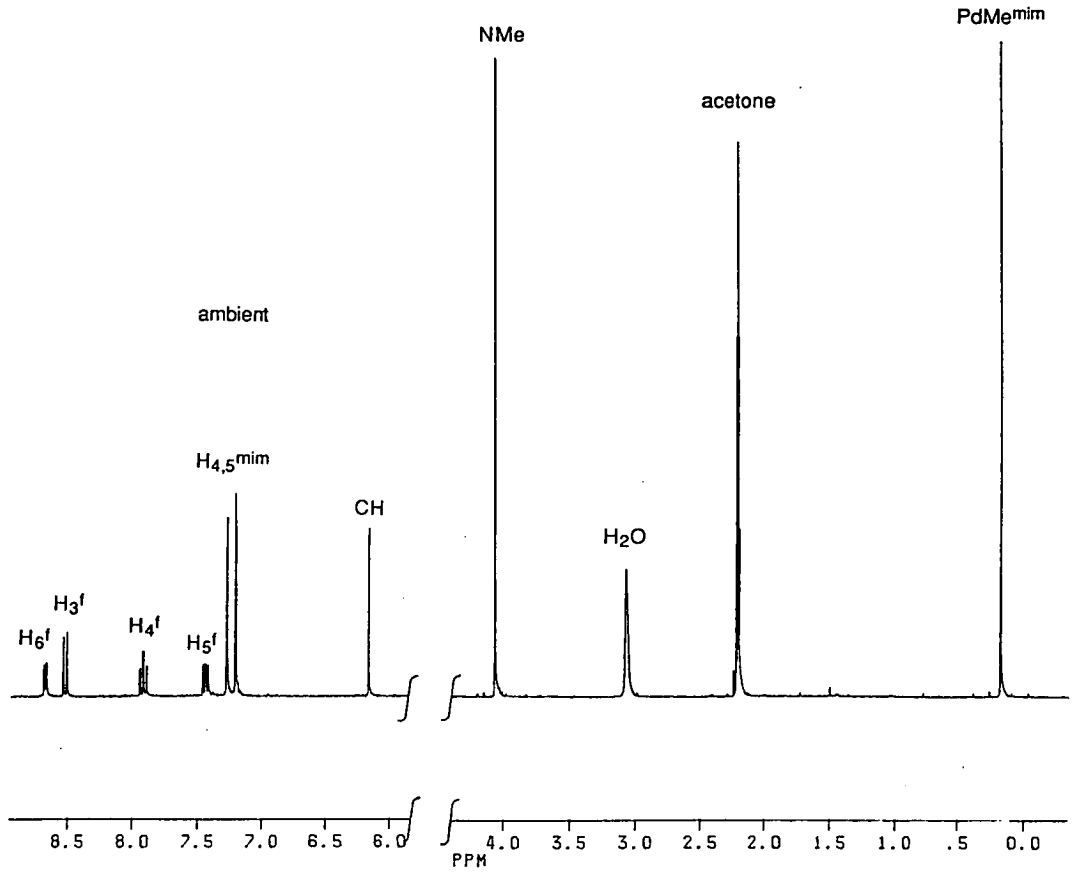
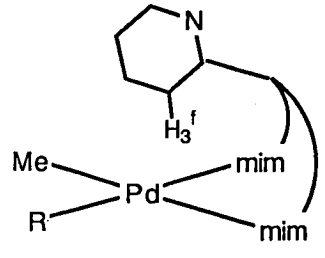


Figure 4.3.2-20.

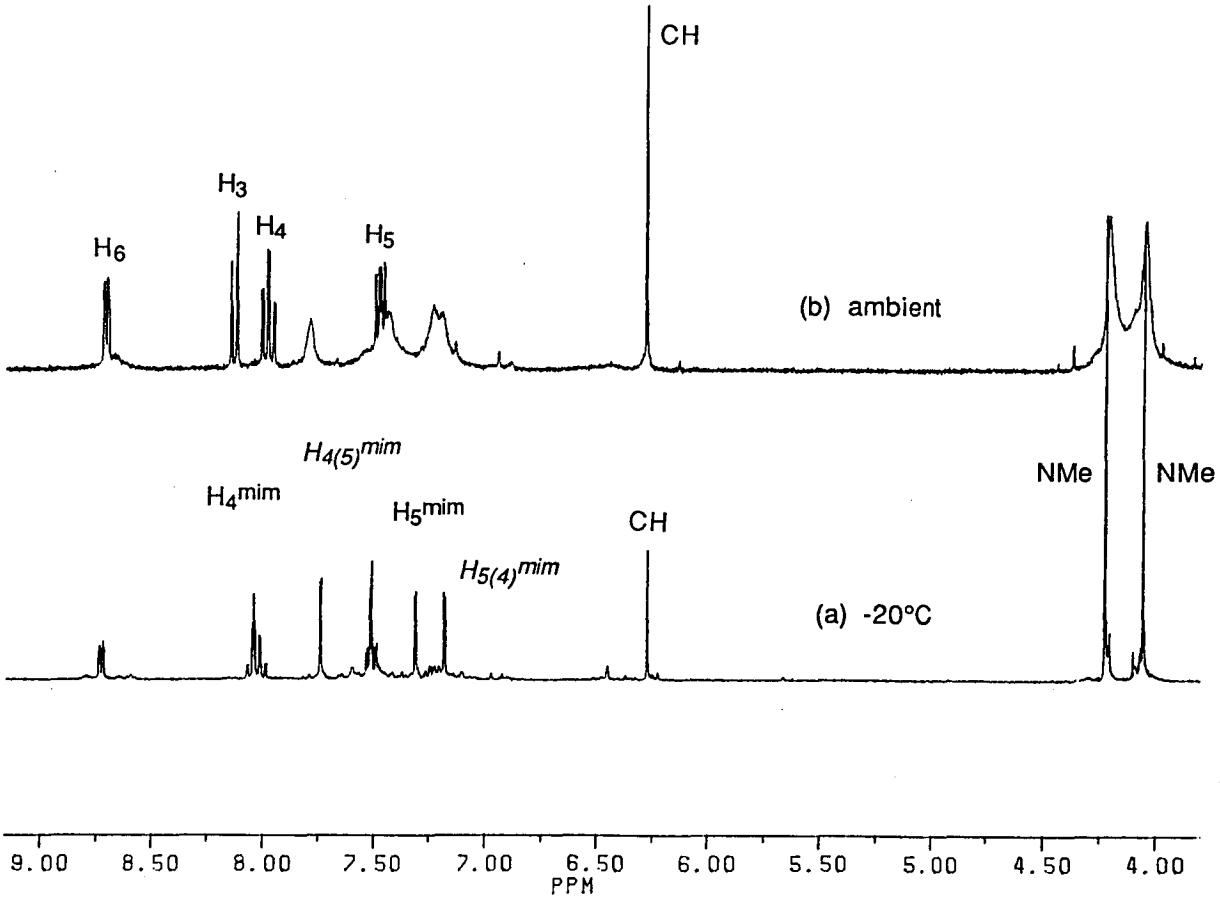


R=Me, I

The low temperature solution state structure of {$PdMeI(pymim_2CH)$} is identical to that for {$PdMe_2(pymim_2CH)$}, figure 4.3.2-20, and was deduced on the same grounds outlined above for {$PdMe_2(pymim_2CH)$}. The presence of other 'spurious' resonances in the baseline may result from conformational isomers with a different orientation of the axial pyridine ring. For example, the low temperature

spectrum displays a resonance at *ca.* 0.22 ppm which is at a position expected for a shielded PdMe group, *i.e.* from an isomer where the axial pyridine ring is orientated parallel to the metal square plane.

Figure 4.3.2-21. Variable Temperature ^{1}H NMR of {PdMeI(pymim$_2$CH)} in Acetone-D6.



4.3.3 {PdMeR(pz$_4$C)} (R=Me,I)

The ambient temperature spectrum of {PdMe$_2$(pz$_4$C)} is displayed in figure 4.3.3-1, and clearly demonstrates that rapid exchange between coordinated and un-coordinated groups occurs. Cooling to -85°C gave spectra displaying four pyrazole environments, figure 4.3.3-2. This is surprising, as only three environments would be expected, a single bound environment, and an axial and equatorial environment. An

explanation for this behaviour is based on the presence of two PdMe resonances at low temperature, and thus the rings *trans* to these groups are inequivalent.

Figure 4.3.3-1. ^{1}H NMR of {$PdMe_2(pz_4CH)$} in Acetone-D6.

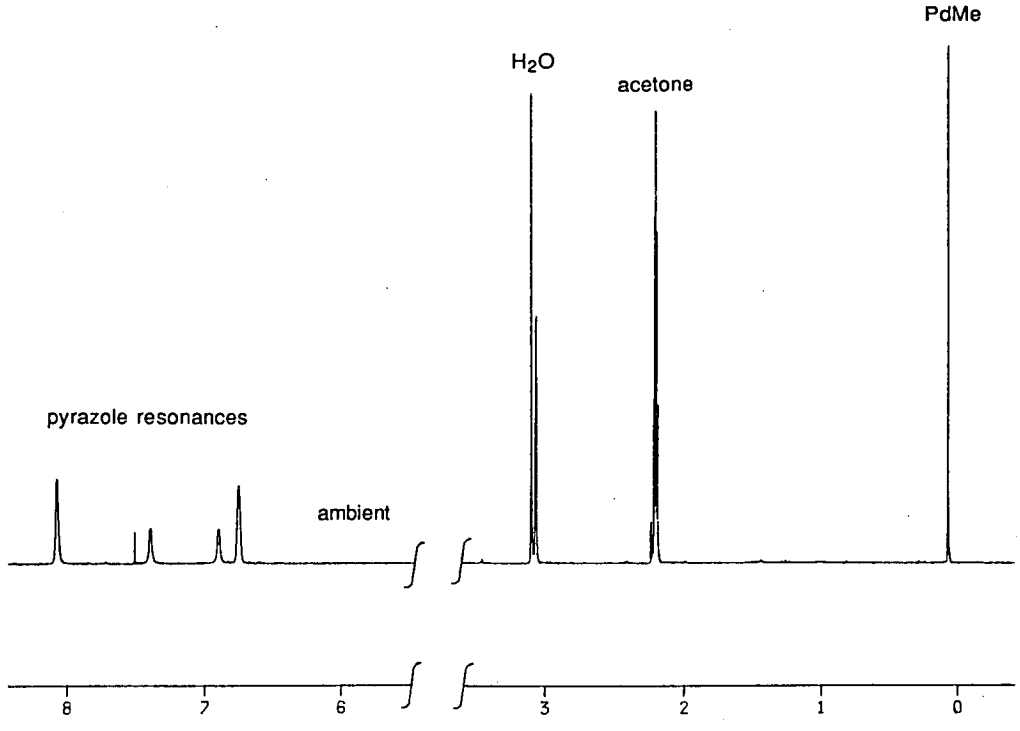
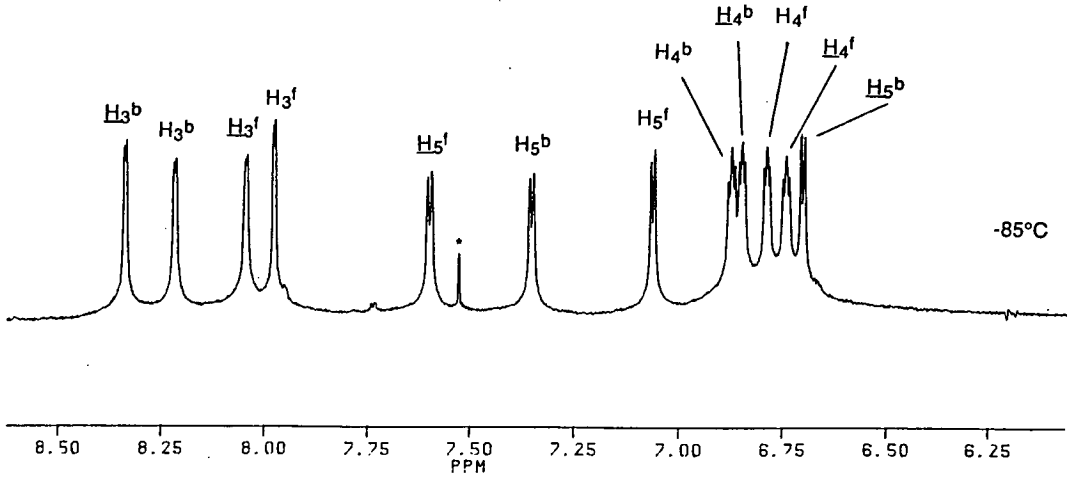


Figure 4.3.3-2. ^{1}H NMR of {$PdMe_2(pz_4CH)$} in Acetone-D6 at -85°C.

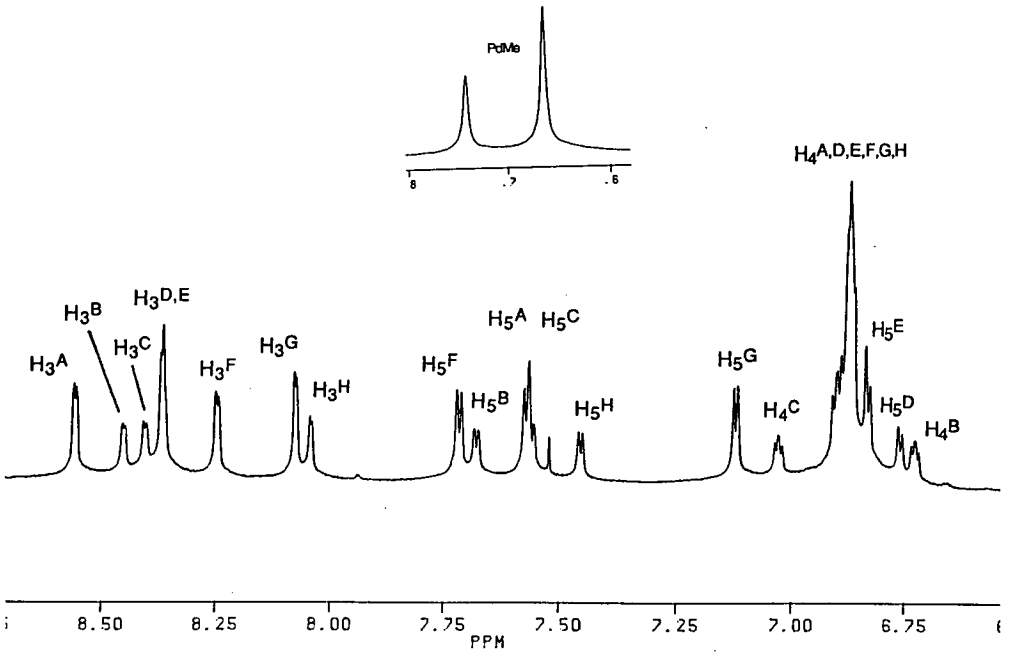


With the aid of a COSY spectrum assignment of protons within each ring system has been achieved but, due to the complexity of the low temperature limiting spectrum, assignment of bound (b) and free (f) donor rings only has been possible, *e.g.* two un-coordinated environments are discerned, and protons within each of these are denoted by H_n^f on $\underline{H}_n^f$. The assignment of bound and free rings is somewhat tentative, and is based on the downfield position of $\underline{H}_3^b$ and H_3^b, and their corresponding H_4 protons, $\underline{H}_4^b$ and H_4^b. The downfield shift is commensurate with that normally observed upon coordination of a ligand to palladium, and the chemical shift position of the $\underline{H}_3^f$ and H_3^f protons are similar to that observed for the free ligand.

In elucidating the structure of the complex, two striking features to note in the low temperature spectrum are that all the H_5 protons appear **upfield** from the H_3 protons, and the PdMe groups are shielded compared with the bidentate analogue $\{PdMe_2(pz_2CH_2)\}$. The position of the H_5 protons with respect to the H_3 protons is the reverse of that normally encountered, and results from shielding by adjacent pyrazole ring(s). Based on this, and noting the shielding of the PdMe groups, a structure containing an axial pyrazole ring parallel to the metal square plane and directed slightly towards a particular methyl group, and an equatorial ring perpendicular to the square plane is suggested.

Further support for this interpretation is obtained upon examination of the low temperature spectrum of the corresponding methyliodo-complex $\{PdMeI(pz_4C)\}$. At low temperature it exhibited a complex spectrum containing 24 resonances, some of which are coincident, and two PdMe resonances in 2:1 ratio, implying two isomers are present, figure 4.3.3-4. Assignment of protons within each isomer, and within each ring system of these isomers, has been possible from integration and a COSY spectrum (chapter 6).

Figure 4.3.3-4. ^1H NMR of {PdMeI(pz_4CH)} in Acetone-D6 at -85°C.



This complex has a similar structure to that for {$PdMe_2(pz_4C)$}, with the shielding cone of the axial pyrazole group directed at the PdMe group, or at the Pd-I group. The major isomer present is assigned as that which contains the axial pyrazole ring directed at the PdMe group. This assignment is based on the upfield position of the PdMe resonance compared with the PdMe resonance of the minor isomer. A similar situation may also occur for {$PdMe_2(pz_4C)$} but, in this instance, both orientations give rise to identical isomers.

4.3.4 Concluding Remarks

The solution state structure(s) for each of the complexes discussed above are displayed together in figure 4.3.4-1, and upon close examination of these structures several conclusionsmay be drawn. Firstly, in complexes containing mixed donor rings, the five membered rings are generally found coordinated to palladium, and for five membered ring systems the more basic *N*-methylimidazole ring is preferred.

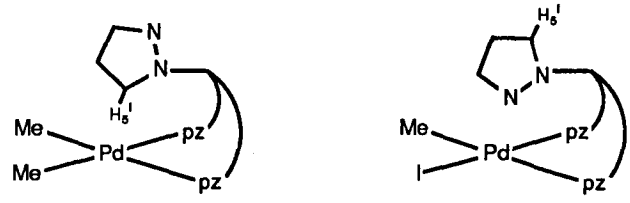
Secondly, all except one complex displayed a preference for orientation of the axial ring either parallel to the metal plane, or perpendicular with the nitrogen lone pair directed away from the palladium centre. For complexes containing coordinated pyridine rings, figure 4.3.4-1a, the former orientation is preferred possibly to avoid close Pd···H or Pd···N interactions. For complexes containing bound pyrazole and/or *N*-methylimidazole rings, figure 4.3.4-1b,c,d,f, the axial group in the latter orientation is preferred, *i.e.* with the axial ring perpendicular to the metal plane, although anomalous behaviour was observed here also, *e.g.* {$PdMe_2(pz_2pyCH)$} has the un-coordinated pyridine ring parallel to the metal plane, while {$PdMe_2(mim_2pyCH)$} has this ring perpendicular to the plane with the H_3 proton adjacent to palladium.

Finally, for complexes where inequivalent donor groups are coordinated to palladium, and the axial group has the H_3 (pyridine) or H_5 (pyrazole) proton adjacent to the palladium centre, it appears that these protons do not lie directly above the palladium centre, but either side of it. This implies that for complexes where identical donor groups are coordinated, the axial proton is positioned similarly but both orientations are in this case equivalent.

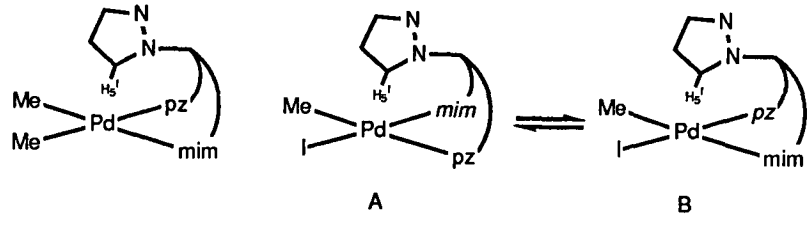
Figure 4.3.4-1.

(a) py_3CH

(b) pz_3CH

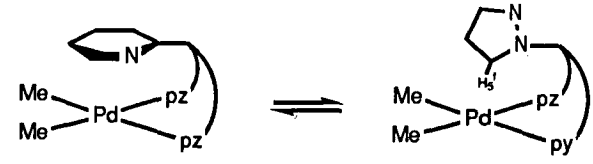


(c) pz_2mimCH

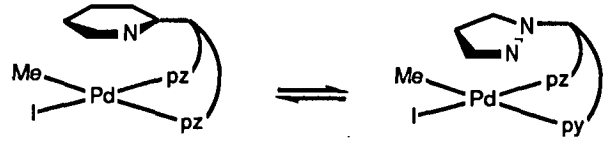


A major isomer B

(d) pz_2pyCH



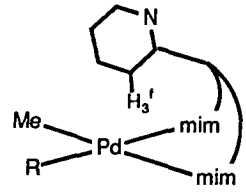
A major isomer B



A major isomer B

(e) py_2mimCH

(f) $pymim_2CH$



R=Me, I

REFERENCES

1. Elguero, J.,
"Pyrazole and their Benzo Derivatives" in "Comprehensive Heterocyclic Chemistry", Katritzky, A.R., and Rees, C.W., (Eds.), Pergamon Press, Oxford, 5 (1984) 167.

2. (a) Grimmett, M.R.
"Imidazoles and their Benzo Derivatives" in Ref 1,5 (1984) 345.
(b) Takeuchi, Y., Yeh, H.J.C., Kirk, K.L., and Cohen, L.A.,
J. Org. Chem., **43** (1978) 3565.

3. Annibale, G., Canovese, L., Cattalini, L., Natile, G., Biagini-Cingi, M., Manotti-Lanfredi, A., and Tiripicchio, A.,
J. Chem. Soc. Dalton Trans., (1981) 2280.

4. Hiraki, K., Fuchita, Y., and Takechi, K.,
Inorg. Chem., **20** (1981) 4316.

5. Polyakov, V.A., and Ryabov, A.D.
J. Chem. Soc. Dalton Trans., (1986) 589.

6. Brookhart, M., and Green, M.L.H.,
J. Organomet. Chem., **250** (1983) 395.

7. Deeming, A.J., Rothwell, I.P., Hursthouse, M.B. and New, L.,
J. Chem. Soc. Dalton Trans., (1978) 1490.

8. Canty, A.J., Minchin, N.J., Skelton, B.W. and White, A.H.
J. Chem. Soc. Dalton Trans., (1987) 1477.

9. Minchin, N.J.,
Ph.D. Thesis, University of Tasmania, 1986.

10. Minghetti, G., Cinellu, M.A., Bandini, A.L., Banditelli, G., Demartin, F., and Manassero, M.,
J. Organomet. Chem., **315** (1986) 387.

11. Canty, A.J., and Marker, A.,
Inorg. Chem., **15** (1976) 425.

12. Minchin, N.J.,

Honours Thesis, University of Tasmania, 1981.

13. Canty, A.J., Minchin, N.J., Healy, P.C., and White, A.H.,

J. Chem. Soc. Dalton Trans., (1982) 1795.

14. Maitlis, P.M.,

"The Organic Chemistry of Palladium", Academic Press, London, 1971.

CHAPTER 5

NEUTRAL AND CATIONIC ALKYLPALLADIUM(IV) COMPLEXES

5.1 INTRODUCTION

Complexes of palladium(IV) are not numerous, although neutral, anionic and cationic complexes are known, *e.g.* PdF_4, $[PdX_6]^{2-}$ (X=F, Cl, Br), $[Pd(S_2CNR_2)_3]^+$ and $\{Pd(S_2CNR_2)_2X_2\}$ (S_2CNR_2=dithiocarbamate).[1] Complexes containing neutral unidentate[2] and polydentate[3,4] ligands are also known, *e.g.* $[NBu_4^n][Pd(py)Cl_5]$[2] in equation 5.1-1 and $\{PdCl_4(bipy)\}$[3] in equation 5.1-2, but are generally less stable, and few have been studied in any detail.

$$[NBu_4^n][Pd(py)Cl_3] + Cl_2 \rightarrow [NBu_4^n][Pd(py)Cl_5] \qquad 5.1\text{-}1$$

$$[PdCl_2(bipy)\} + Cl_2 \rightarrow \{PdCl_4(bipy)\} \qquad 5.1\text{-}2$$

As this thesis is concerned primarily with the organometallic chemistry of palladium, inorganic derivatives are not discussed further, and the reader is referred to several monographs on the subject,[5] and a recent review.[1]

Organometallic complexes of palladium in the tetravalent state are extremely rare. Indeed, up to the commencement of this study, only seven unambiguously characterised complexes containing a Pd(IV)-C σ bond have been reported,[6] all containing the stabilising ligand C_6F_5. These complexes were prepared by Uson *et.al.*[7,8] by bubbling Cl_2 through a solution of the corresponding palladium(II) complex, equations 5.1-3,4.

$$\{Pd(C_6F_5)_2(chel)\} + Cl_2 \rightarrow \{Pd(C_6F_5)_2Cl_2(chel)\} \qquad 5.1\text{-}3$$

chel=bipy, phen, en, pn (=propylenediamine)

$$\{Pd(C_6F_5)Cl(chel)\} + Cl_2 \rightarrow \{Pd(C_6F_5)Cl_3(chel)\} \qquad 5.1\text{-}4$$

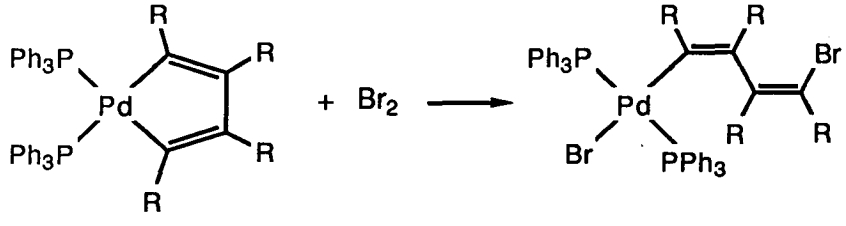
chel=bipy, phen, tmeda

Characterisation was accomplished by infrared spectroscopy, and from the observation that solutions of the complexes oxidised iodide to iodine, a feature not

observed for the palladium(II) precursors. Further, upon heating, the complexes $\{Pd(C_6F_5)Cl_3(chel)\}$ eliminate Cl_2,[8] and treatment of $\{Pd(C_6F_5)_2Cl_2(chel)\}$ with an excess of Cl_2 results in cleavage of the C_6F_5 group, to produce the known inorganic complexes $\{PdCl_4(chel)\}$,[7] equation 5.1-5. Cleavage of palladium-carbon σ bonds by treatment with halogen is known,[6] *e.g.* equation 5.1-6.[9]

$$\{PdCl_2(chel)\} + \text{xs } Cl_2 \rightarrow \{PdCl_4(chel)\} \qquad 5.1\text{-}5$$

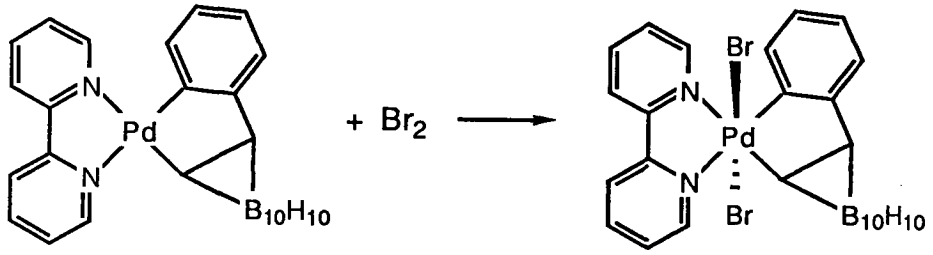
chel=bipy, phen, en, pn.



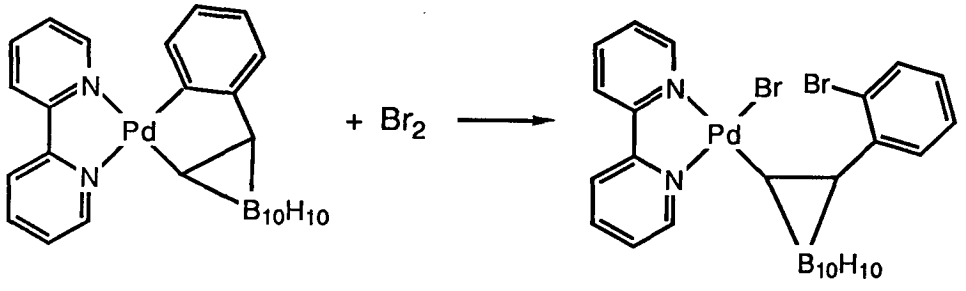
5.1-6

Preparation of the organopalladium(IV) complexes $\{Pd(C_6F_5)_2Cl_2(PPh_3)_2\}$[10,11] and $\{Pd(C_6F_5)Cl_3(PPh_3)_2\}$,[12] containing phosphine based ligands, has been reported, although attempts to repeat these preparations have failed,[13] and formulation as Pd(IV) complexes is considered incorrect.[13] This is consistent with the general observation that inorganic Pd(IV) complexes containing phosphine based ligands are less stable than those containing nitrogen-donor ligands,[2,3a] and the paucity of inorganic Pd(IV) complexes containing phosphorous-based ligands, compared with nitrogen-based ligands.

Similarly, the only other organopalladium(IV) complex which has been reported,[14] and prepared according to equation 5.1-7, is now considered incorrect.[6] Zakharkin and Kovredov proposed this formulation based solely on an elemental analysis, and noted that the complex was stable in air and decomposed at 203-205°C. In view of the stability of the complex the alternative formulation depicted in equation 5.1-8 has now been proposed,[6] but the formation of a transient Pd(IV) intermediate cannot be discounted.



5.1-7

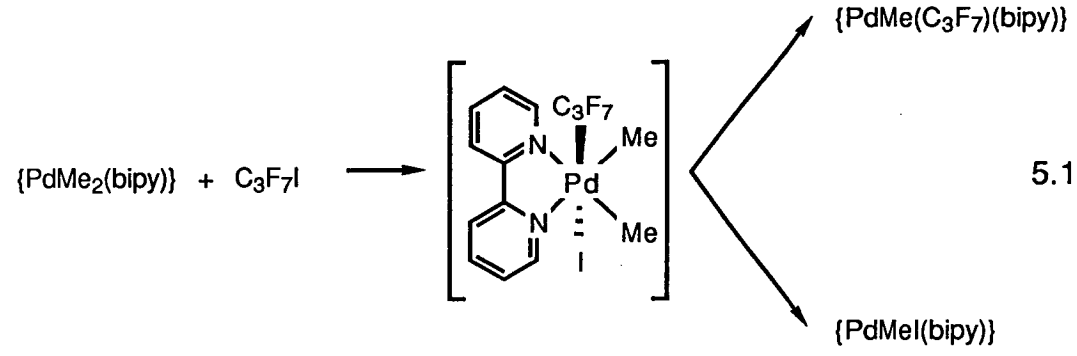


5.1-8

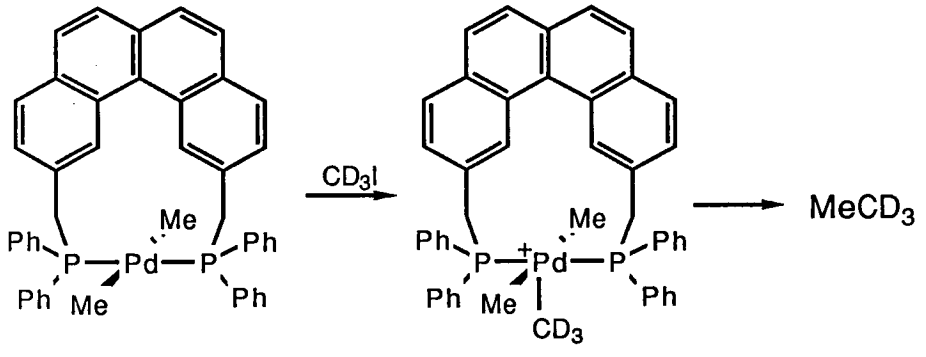
While authentic examples of Pd(IV) complexes containing a Pd-C σ bond are limited, organopalladium(IV) complexes have been implicated as intermediates in numerous reactions and catalytic processes.[6,15-21] For example, a Pd(IV) intermediate has been proposed for the reaction of C_3F_7I with {$PdMe_2$(bipy)},[17] equation 5.1-9, and for the reaction of CD_3I with {$PdMe_2$(transphos)},[20C] equation 5.1-10. These intermediates were not detected, and the proposal of Pd(IV) intermediacy is generally based on the reaction products obtained.

An exception to this has been reported by Weinberg *et. al.*,[21] who have reported the spectroscopic detection of a possible Pd(IV) intermediate (Pd^{IV}-Me=2.20 ppm) upon oxidative addition of MeI to (I), equation 5.1-11. A complex mixture of products was obtained, which could not be satisfactorily identified, although significant quantities of MeCl were found, consistent with reductive elimination from a Pd(IV) intermediate.[21]

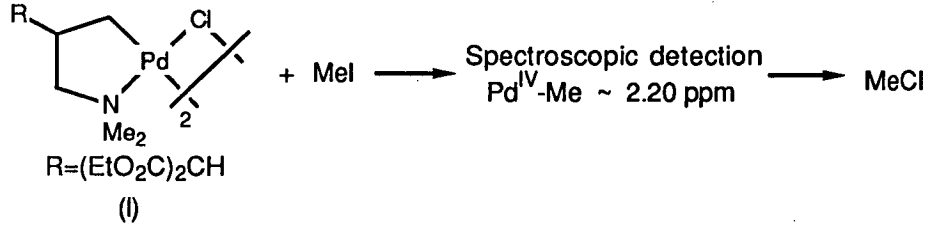
The paucity of isolated organometallic, and indeed inorganic, palladium(IV) complexes compared with its d^6 congener platinum is striking, and has been attributed to the fact that the sum of the first four ionisation potentials of palladium (109 eV) is



5.1-9



5.1-10



5.1-11

greater than that of platinum (97.16 eV).[5b] The chemistry of the platinum group metals in higher oxidation states has been summarised in several recent reviews.[22,23]

5.2 CROSS COUPLING REACTIONS

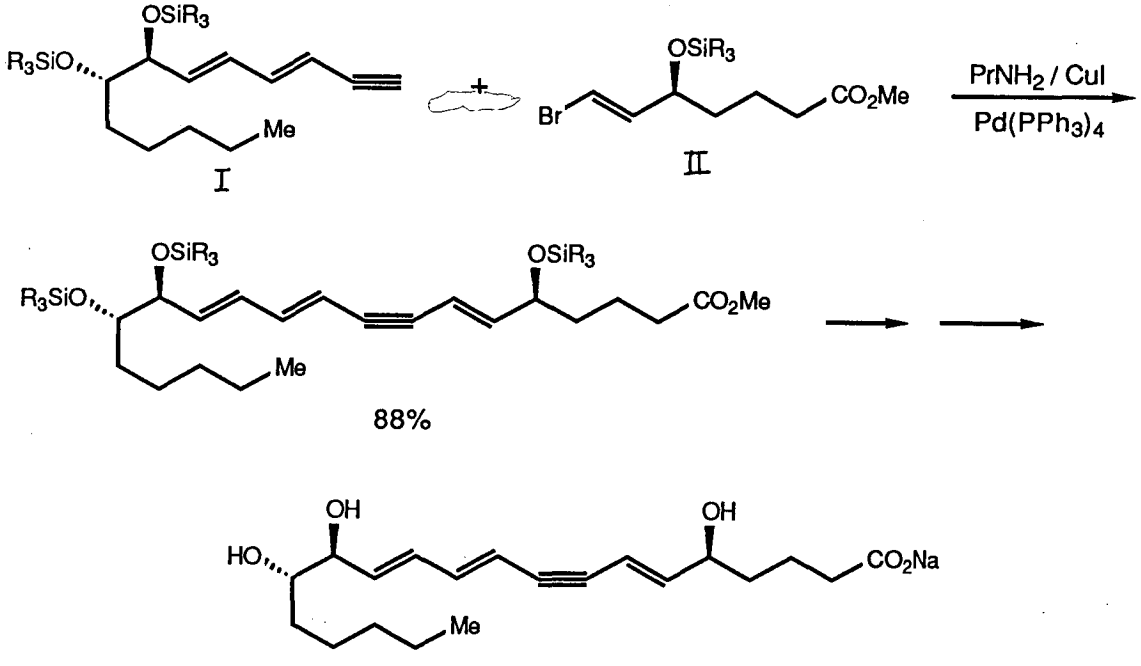
5.2.1 Introduction

The formation of C-C σ bond is one of the most important reactions in organic synthesis, and the palladium catalysed coupling of an organohalide (RX) with an organometal (R'M) represents an attractive and synthetically useful procedure for the formation of such bonds, equation 5.2.1-1. For example, the total synthesis of

Lipoxin B has been reported recently,[24] and the cross coupling of (I) with (II) in equation 5.2.1-2 gave the Lipoxin B skeleton in 88% yield. In this case the organometal is an alkenyl cuprate generated *in situ* by reaction of (I) with base ($PrNH_2$) and a copper (I) salt.

$$RX + R'M \rightarrow R\text{-}R' + MX \qquad 5.2.1\text{-}1$$

Equation 5.2.1-2.



Lipoxin B

For cross coupling reactions the palladium catalyst used almost invariably contains phosphine based ligands, *e.g.* $\{Pd(PPh_3)_4\}$,[25-31] $\{PdCl_2(L_2))\}$ ($L=PPh_3$,[29,32] dppe[27,33]), $\{PdRX(PPh_3)_2\}$ ($R=PhCh_2$, $X=Cl$;[25,34,35] $R=Ph$, $X=I$[36,37]), and $\{PdCl_2(dppf^{\dagger})\}$,[27,33] or less frequently nitrogen based ligands, *e.g.* $\{PdCl_2(MeCN)_2\}$,[30,38,39] and $\{PdEt_2(bipy)\}$.[40]

---

† dppf= 1,1'-bis(diphenylphosphino)ferrocene.

The use of 'Pd-PPh_3' catalysts is extensive,[41] and a 14 electron species, '$Pd(PPh_3)_2$', has been implicated as the species undergoing oxidation addition with organohalides.[42] The attainment of a coordinatively unsaturated intermediate is readily achieved by $\{Pd(PPh_3)_4\}$, which dissociates in solution according to the equilibria in equation 5.2.1-3.[43] For complexes of the form $\{PdCl_2(PPh_3)_2\}$ and $\{PdRX(PPh_3)_2\}$ the active intermediate is accessible upon reaction with the organometal, followed by reductive elimination *e.g.* equation 5.2.1-4.[44] In this instance, however, the exact nature of the intermediate is unknown, although reaction of RLi with $\{PdCl_2(PPh_3)_2\}$ has been proposed to give complexes of the form $LiXPd(PPh_3)_2$, $Li_2X_2Pd(PPh_3)_2$, and aggregates thereof. [44]

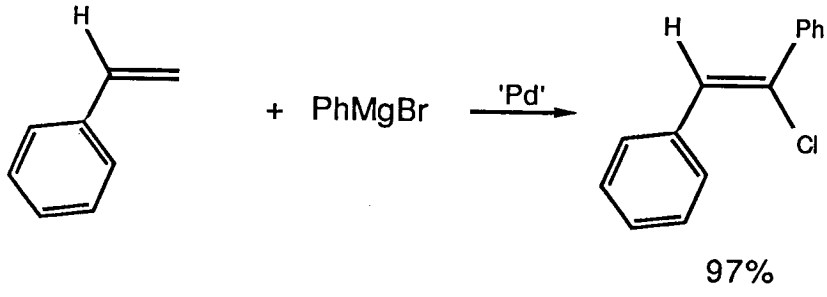
$$\{Pd(PPh_3)_4\} \leftrightarrow \{Pd(PPh_3)_3\} + PPh_3$$
$$\{Pd(PPh_3)_3\} \leftrightarrow \{Pd(PPh_3)_2\} + PPh_3 \qquad 5.2.1\text{-}3$$

$$\{PdCl_2(PPh_3)_2\} + 2\,PhLi \rightarrow 'Pd(PPh_3)_2' + PhPh \qquad 5.2.1\text{-}4$$

The range of organometals used is also extensive, with organometallic reagents containing Cu,[24,37,41] Mg,[27,36,45,46] Pb,[25] B,[26] Zr,[47,48] Zn,[28,33,48] and Sn[30,49,50] entering into the palladium cross coupling reaction. Similarly, the range of organohalides is extremely diverse. It is notable that one requirement of both the organohalide and the organometallic reagent is that they do not contain β-hydrogens, to avoid β-hydrogen elimination, although several successful cross coupling reactions with organohalides and organometals containing β-hydrogens have been reported recently.[40,51]

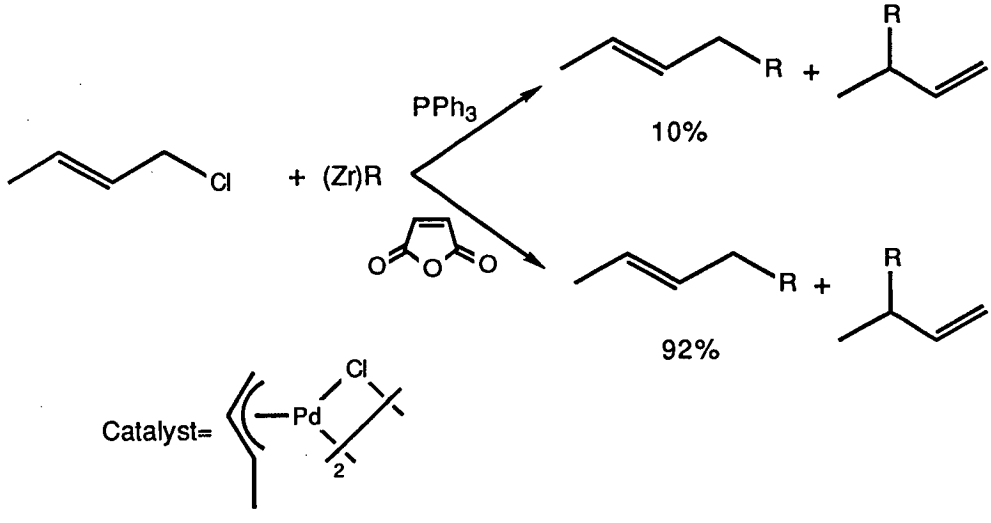
Finally, the cross coupling of organohalides and organometals frequently proceeds with a high degree of regio- and stereospecificity, for example the monoalkylation and -arylation of 1,1-dichloro-1-alkenes by Grignard or organozinc reagents in the presence of $\{PdCl_2(PPh_2(CH_2)_4PPh_2)\}$, equation 5.2.1-5,[46] and often regio control can be achieved by subtle changes in the reaction conditions, *e.g.* equation 5.2.1-6.[47] Further, it is interesting to note that Negishi *et. al.*[48] have found that in cross coupling of alkenylmetals (M=Zn, Zr, Al) with aryl- and alkenylhalides

(X=Br, I), palladium catalysts permitted 100% stereospecificity whereas nickel catalysts lead to partial stereochemical scrambling, *e.g.* equation 5.2.1-7.[48]

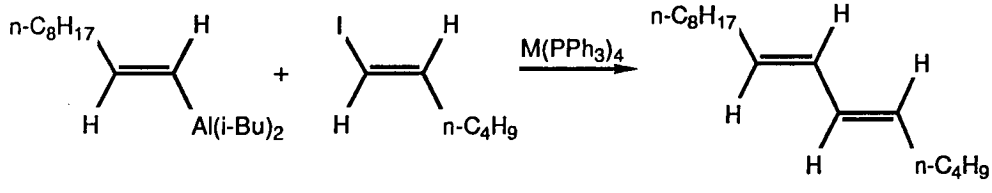


97%

5.2.1-5



5.2.1-6



5.2.1-7

M=Ni , 72% (95% E,E)
M=Pd , 75% (>98% E,E)

5.2.2 Mechanisms for the Cross Coupling Reaction

Several mechanisms for the metal catalysed cross coupling of organohalides with organometals have been proposed. All involve, at some stage in the catalytic cycle, *oxidative addition* of the organohalide and *reductive elimination* of the coupled product.[52]

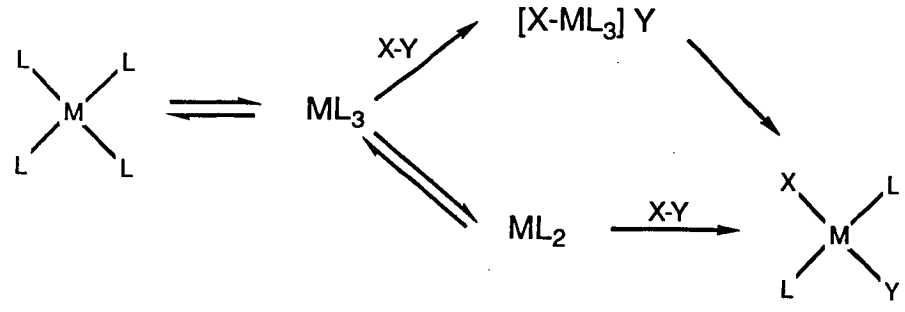
(a) Oxidative Addition

Oxidative addition is the term used to describe, without implication of mechanism, the oxidation of a metal by a substrate X-Y, and very frequently the increase in oxidation state is accompanied by an increase in coordination number. Both two- and one-electron oxidative additions are recognised, equation 5.2.2-1,2 respectively. In the former the metal increases its oxidation state from n to (n+2), while in the later an increase from n to (n+1) occurs, although in either case an overall two-electron change results, *i.e.* M^n to M^{n+2} or $2M^n$ to $2M^{n+1}$

$$M^n + X\text{-}Y \rightarrow X\text{-}M^{n+2}\text{-}Y \qquad 5.2.2\text{-}1$$

$$2M^n + X\text{-}Y \rightarrow M^{n+1}\text{-}X + M^{n+1}\text{-}Y \qquad 5.2.2\text{-}2$$

Characteristic of group 8 metals with the d^8 and d^{10} electronic configuration is their propensity to undergo oxidative addition reactions, and several factors are important in determining the ability of a metal to participate in these reactions. Firstly, the transition metal must be in a low valent state, and unlike the group 1 and 2 metals which react in bulk, group 8 metals must be in the atomic state, generally through complexation with ligands. Secondly, the coordination number of the metal is important, and there is much evidence that an 18 electron d^{10} square planar complex undergoes ligand dissociation to form coordinatively unsaturated intermediates, *e.g.* the complexes $\{M(PPh_3)_4\}$ (M=Ni, Pd, Pt) undergo ligand dissociation to form two and three coordinate intermediates which are reactive towards oxidative addition, equation 5.2.2-3.



5.2.2-3

Finally, the ligands coordinated are also important in determining the reactivity of the metal complex. The presence of phosphine ligands, which are σ-donors (lone pair donation), *increases* the electron density at the metal and hence increases the nucleophicity of the metal, while at the same time increases the tendency for phosphine dissociation.[52] Carbon monoxide, on the other hand, is a π-acceptor ligand, and *decreases* the electron density at the metal, thus lowering the nucleophicity of the metal and lowering the tendency for phosphine dissociation.[52] There is good evidence, however, that steric effects are much more important than electronic effects in determining the dissociation of phosphine ligands, and the increasing size of the ligand cone has been equated to an increased tendency for phosphine dissociation.[52]

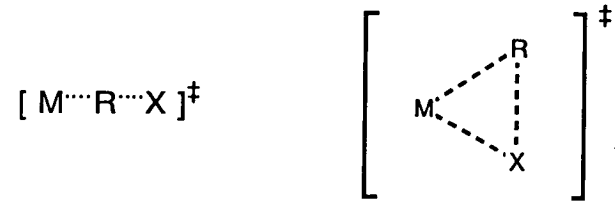
Generally, the reactivity of group 8 metals toward oxidative addition increases in going from right to left in the periodic table, in going down a particular group in the table, and in decreasing the initial oxidation number.

The substrates X-Y which add by oxidative addition can be divided into three broad groups: *Class A*, nonpolar species, *e.g.* H_2; *Class B*, polar electrophilic species, *e.g.* RX; and *Class C*, multiply bonded species, *e.g.* O_2, which remain joined by one or more X-Y bonds in the adduct. Further, two types of mechanisms have been proposed for the oxidative addition of X-Y to metal complexes, concerted two equivalent or successive one equivalent transformations, and both are considered below.

Two Electron Mechanisms

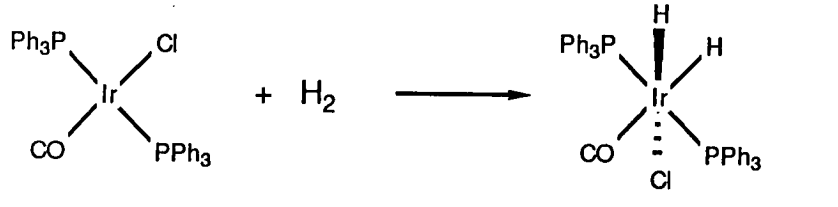
The concerted process for oxidative addition of alkylhalides may involve nucleophilic displacement of halide by attack of the metal at the carbon centre, and may proceed *via* a two- or three-centre transition state, figure 5.2.2-1a,b respectively.

Figure 5.2.2-1.



(a) (b)

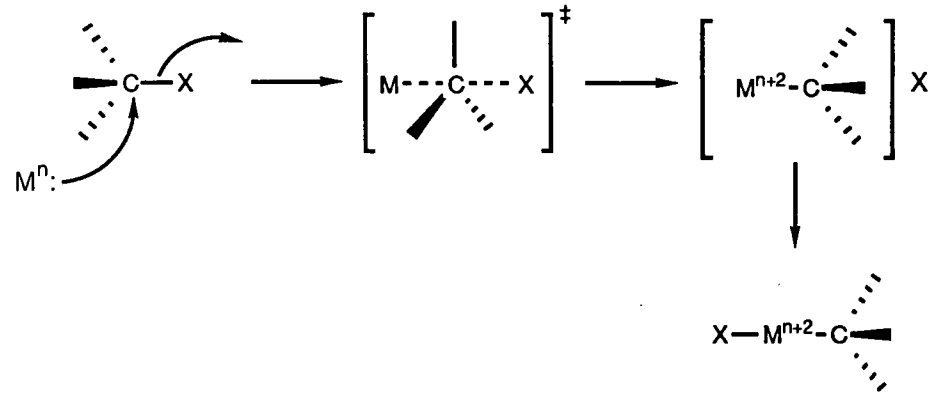
A cyclic, or 3-centre, transition state has been established for oxidative addition of H_2 and RH,[53] *e.g.* equation 5.2.2-4, and although suggested for polar electrophilic substrates has never been conclusively demonstrated. It is expected that concerted processes proceeding *via* 3 centred transition states would lead to retention of configuration at chiral carbon.



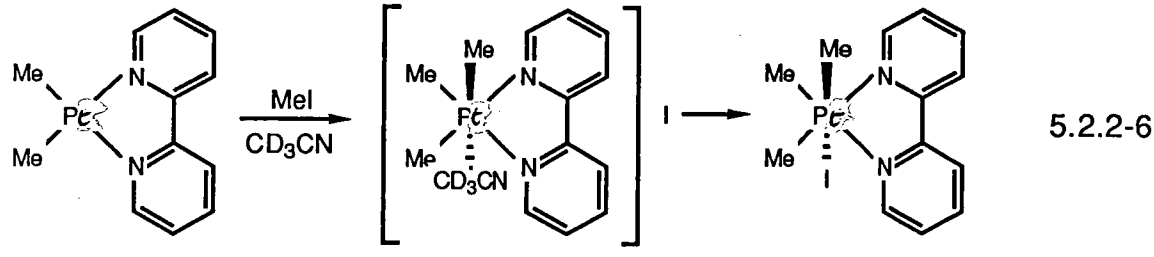
5.2.2-4

The alternative mechanism, *i.e.* that proceeding *via* a two-centre transition state, is analogous to the classical S_N2 mechanism for the hydrolysis of MeBr,[54] and employs the metal centre as the nucleophile.[55] The reaction proceeds *via* the formation of a cationic intermediate, followed by collapse of the ion pair, equation 5.2.2-5.[55] The cationic intermediate has in some cases been detected,[56] equation 5.2.2-6.[56a] Important characteristics of this oxidative addition mechanism are: inversion of configuration of chiral carbon, second order kinetics, *i.e.* first order in both alkylhalide

and the metal complex, and classical RX reactivity patterns, *i.e.* Me > 1° > 2° > 3° and I > Br > Cl >> F.



5.2.2-5



5.2.2-6

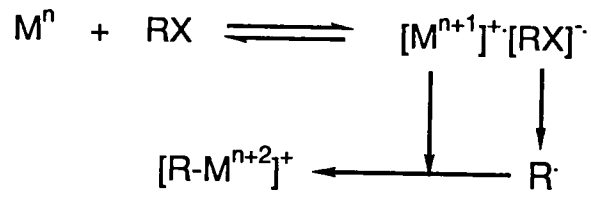
One Electron Mechanisms

Both chain and non-chain free radical mechanisms have been established for oxidative addition reactions which occur *via* radical intermediates, scheme 5.2.2-1,2 respectively.

Scheme 5.2.2-1.

In· + X-R → In-X + R·		initiation
R· + M^n → R-M^{n+1}		
R-M^{n+1} + X-R → R-M^{n+2}-X + R·		propagation
2R· ⟶	side products	termination
R· + M· ⟶		

Scheme 5.2.2-2.



Important characteristics of radical mechanisms are racemisation of configuration at chiral carbon, and for various organohalides the order of reactivity I > Br > Cl, which is that found for the S_N2 mechanism, and 3° > 2° > 1° , which is the *reverse* of that found for S_N2 reactions, has been established. Also the observation of CIDNP, detection of radicals by E.S.R., and radical trapping experiments, *e.g.* with Bu^{t}NO, provides strong evidence for radical intermediacy. Care must be exercised in interpretation of results as detection of radicals by, for example, E.S.R. does not prove that a radical reaction is the **main** reaction pathway. A more detailed discussion of the role of free radicals in oxidative addition can be found elsewhere.[52,57]

For the oxidative addition of organohalides to d^{10} palladium(0) substrates, remarkably few definitive mechanistic studies have been reported. This is surprising considering the important role palladium plays in a variety of stoichiometric and catalytic reactions.[58] However, from those studies reported it is clear that palladium can participate in several different mechanistic pathways, which differ only slightly in energy, depending upon the organic halide, and the ligands coordinated to palladium. For example, *i*-propyliodide has been reported to react with $\{Pd(PEt_3)_3\}$ by a radical mechanism,[59] whereas benzyl-α-d chloride reacts with $\{Pd(PPh_3)_4\}$ and $\{Pd(PEt_3)_3\}$ by an S_N2 mechanism.[60]

(b) Reductive Elimination

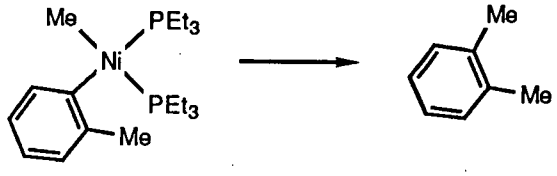
Reduction elimination is the reverse of oxidative addition. Equation 5.2.2-7 portrays the elimination of two ligands from a single metal, while equation 5.2.2-8 portrays the elimination of two ligands from two metal centres, and in either case an overall two electron change occurs. The former elimination is particularly important as

it represents the final step in many homogeneously catalysed reactions, and further discussion is restricted to this mechanism.

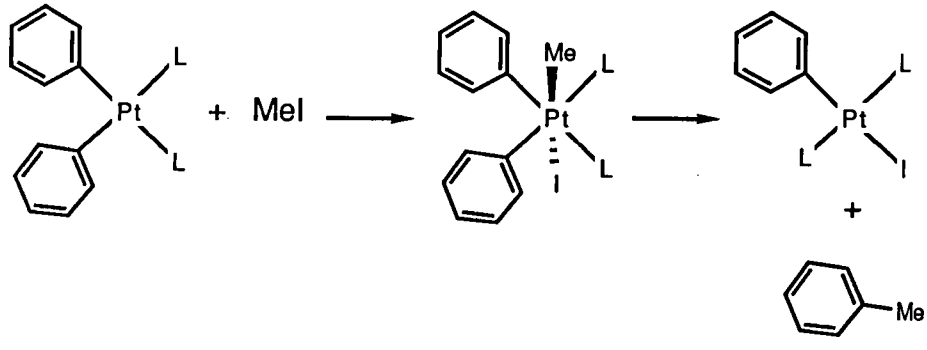
$$X\text{-}M^{n+2}\text{-}Y \rightarrow M^{n} + X\text{-}Y \qquad 5.2.2\text{-}7$$

$$M^{n+1}\text{-}X + M^{n+1}\text{-}Y \rightarrow 2M^{n} + X\text{-}Y \qquad 5.2.2\text{-}8$$

The elimination of two ligands from a common metal centre is also termed *1,1-reductive elimination,* and is obviously confined to those metals having stable oxidation states which differ by two. In 1,1-reductive elimination reactions both the oxidation state and coordination number are reduced by two. The process is concerted, *i.e.* bond making accompanies bond breaking, and no high energy intermediates such as free radicals are involved. The oxidative addition-reductive elimination sequence is involved in both stoichiometric and catalytic coupling reactions, *e.g.* equation 5.2.2-9,[61] 10.[62]



5.2.2-9

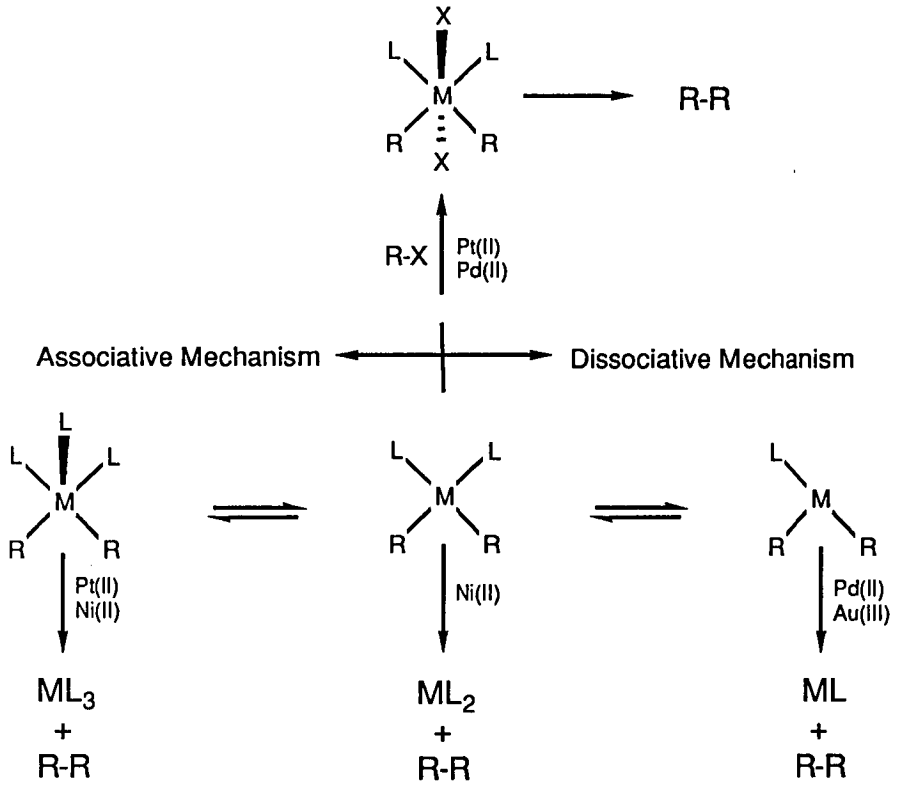


5.2.2-10

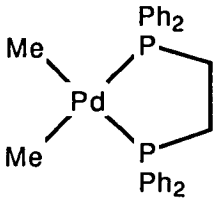
A summary of the various 1,1-reductive elimination pathways for the d^8 metals Ni(II), Pd(II), Pt(II) and Au(III) shows that apart from elimination from square planar four coordinate complexes, both associative and dissociative pathways are available, scheme 5.2.2-3. Despite the degree of coordinative saturation displayed by the metals

an important pre-requisite for 1,1-reductive elimination is that coupling groups are adjacent, *i.e.* occupy positions *cis* to each other, *e.g.* {$PdMe_2$(dppe)} eliminates ethane in DMSO at 80°C, equation 5.2.2-11, but {$PdMe_2$(transphos)} fails to undergo reductive elimination of ethane,[20c] equation 5.2.2-12. This requirement carries the implication that *trans* complexes must first undergo *cis*⇌*trans* isomerism prior to reductive elimination, [20c] equation 5.2.2-13.

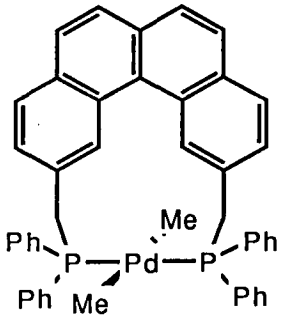
Scheme 5.2.2-3.



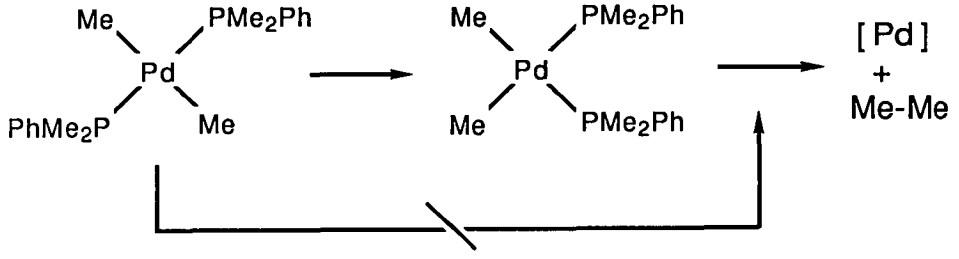
Solutions containing equimolar quantities of *cis*-{$Pd(CH_3)_2(L_2)$} and *cis*-{$Pd(CD_3)_2(L_2)$} {L_2=$2PPh_3$, $2PMePh_2$, dppe) undergo reductive elimination to produce CH_3CH_3 and CD_3CD_3, equation 5.2.2-14.[20c] No CD_3CH_3 could be detected demonstrating CH_3 for CD_3 exchange does not occur, and that reductive elimination is mononuclear and intramolecular.[20d]



$$\xrightarrow[80^{\circ}C]{DMSO} \quad [Pd] + Me\text{-}Me \qquad 5.2.2\text{-}11$$



$$\not\longrightarrow \quad [Pd] + Me\text{-}Me \qquad 5.2.2\text{-}12$$



5.2.2-13

$$cis\text{-}\{Pd(CH_3)_2(L_2)\} + cis\text{-}\{Pd(CD_3)_2(L_2)\} \rightarrow CH_3CH_3 + CD_3CD_3 \qquad 5.2.2\text{-}14$$

L_2=2PPh$_3$, 2PMePh$_2$,dppe.

Kinetic studies for the reductive elimination of ethane from the complexes $\{PdMe_2(L_2)\}$ (L_2=2PPh$_3$,[20c] 2PMePh$_2$[20c,e], dppe[20c]) reveal that first order kinetics are obeyed, and that the rate constant parallels the ability of the complex to dissociate phosphine. Further, added phosphine retarded the rate of ethane elimination, and also consistent with a dissociative mechanism is the observation that the complex $\{PdMe_2(dppe)\}$, containing the *cis* chelating ligand dppe, eliminates ethane 50-100 times slower than $\{PdMe_2(PMePh_2)\}$, equation 5.2.2-15. Reductive elimination from either a Y or T shaped intermediate was proposed.[20e]

$$\{PdMe_2(L_2)\} \longrightarrow \{PdMe_2(L)\} \xrightarrow{K_1} [Pd] + Me\text{-}Me \qquad 5.2.2\text{-}15$$

$$+ L,\ rate < K_1$$

Theoretical calculations support reductive elimination *via* a dissociative mechanism, and from a Y or T shaped intermediate.[63] From these calculations several other important conclusions emerged:

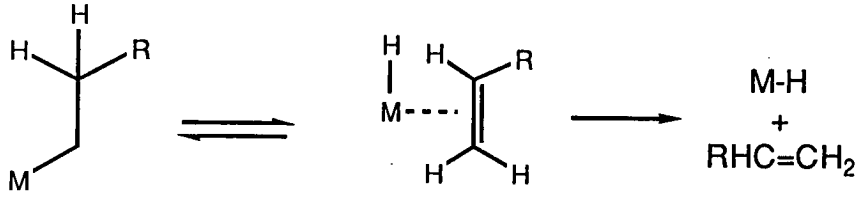
(1) the better the σ-donating capability of the leaving group the more facile the elimination;

(2) stronger donor ligands *trans* to the leaving groups increases the barrier to elimination;

(3) the reductive elimination barrier is controlled by the energy of the antisymmetric b_2 orbital; and

(4) the barrier for isomerisation from one T shaped geometry to another is substantial, and much higher than the energy barrier for reductive elimination from either a Y or T shaped complex.[63]

A second important decomposition route for palladium complexes with organic ligands which contain β-hydrogens is β-*hydrogen elimination*,[64,65] equation 5.2.2-16. Other decomposition routes are also available to palladium and include α-*hydrogen elimination*,[20b] and *homolysis* of the M-C bond to produce R· radicals.[66,52]



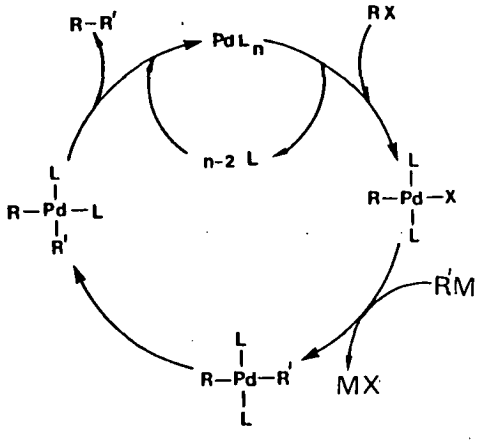
5.2.2-16

A frequently proposed mechanism for the palladium catalysed coupling of an organohalide (RX) with an organometal (R'M), equation 5.2.2-17, is described by the cycle depicted in scheme 5.2.2-4. A similar cycle has been proposed for the related carbonylative coupling reaction, *i.e.* equation 5.2.2-18 and scheme 5.2.2-5.[49]

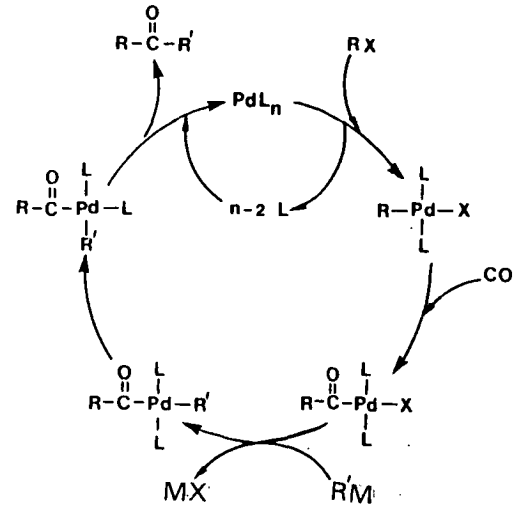
$$RX + R'M \xrightarrow{Pd} R\text{-}R' + MX \qquad 5.2.2\text{-}17$$

$$RX + R'M \xrightarrow[CO]{Pd} R\text{-}(CO)\text{-}R' + MX \qquad 5.3.3\text{-}18$$

Scheme 5.2.2-4.



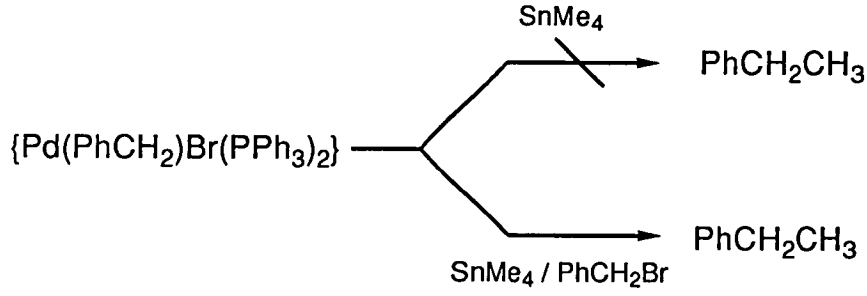
Scheme 5.2.2-5.



The cycle, commencing from $\{PdL_n\}$, involves oxidative addition of RX, followed by metathesis of the halide with R'M to produce the diorgano intermediate PdRR', followed by *cis-trans* isomerism if necessary, and 1,1-reductive elimination of R-R'. The cycle essentially involves the sequence *oxidative addition-transmetallation-reductive elimination*, and while isolation of products at each stage of the cycle is, in a catalytic experiment, not possible, each of the individual steps has been extensively studied in stoichiometric reactions.[67]

The cycle as drawn, however, fails to explain the frequent production of homocoupled products, RR, and the observation that often the entire catalytic cycle is faster, than expected from the rate of reductive elimination from $\{PdRR'(L_2)\}$. For example, the reaction of $\{Pd(CH_2Ph)Br(PPh_3)_2\}$ with $SnMe_4$ produced only minor quantities of ethyl benzene, but in the presence of an excess of benzylhalide a considerable increase in the yield of ethylbenzene was observed,[20b] equation 5.2.2-19. Further, while thermolysis of $\{PdMe_2(PPh_3)_2\}$ produced ethane only,[20c] equation 5.2.2-20, reaction of $\{PdMe_2(PPh_3)_2\}$ with benzylbromide produced mostly ethyl benzene together with a small amount of ethane,[20b] equation 5.2.2-21. These results support the formation of a transient Pd(IV) intermediate which undergoes facile

reductive elimination, and leads to the proposal that Pd(IV) intermediates may participate in the cross coupling reaction,[20c] scheme 5.2.2-6.

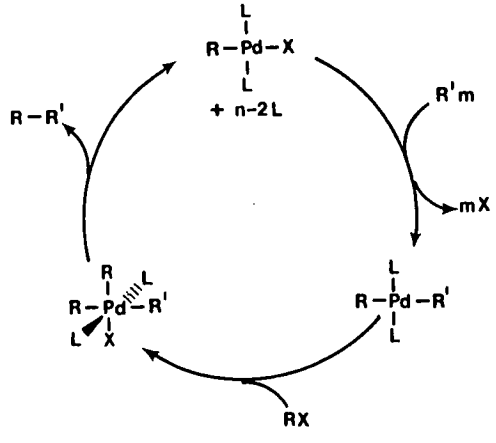


5.2.2-19

$$\{PdMe_2(PPh_3)_2\} \xrightarrow{\Delta} Me\text{-}Me + [Pd] \qquad 5.2.2\text{-}20$$

$$\{PdMe_2(PPh_3)_2\} \xrightarrow{PhCH_2Br} PhCH_2CH_3 \ (+ \ MeMe) \qquad 5.2.2\text{-}21$$

Scheme 5.2.2-6.

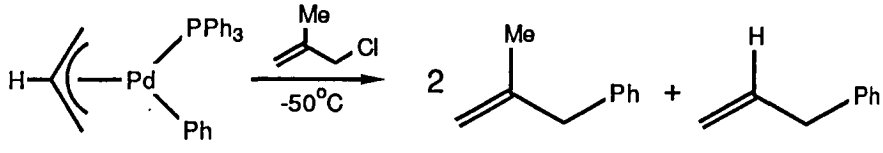


Although the participation of Pd(IV) intermediates explains the presence of homocoupled products and the observed increase in the rate of reductive elimination in the presence of organohalides, palladium(IV) complexes containing alkyl groups have never been isolated. Compelling evidence for their existence, however, is obtained upon the reaction of {$PdMe_2$(transphos)} with CH_3I and CD_3I. The complex {$PdMe_2$(transphos)} fails to eliminate ethane even under severe conditions, equation

5.2.2-12, but in the presence of CH_3I and CD_3I readily eliminates CH_3CH_3 and CH_3CD_3 respectively,[20c] equation 5.1-10.

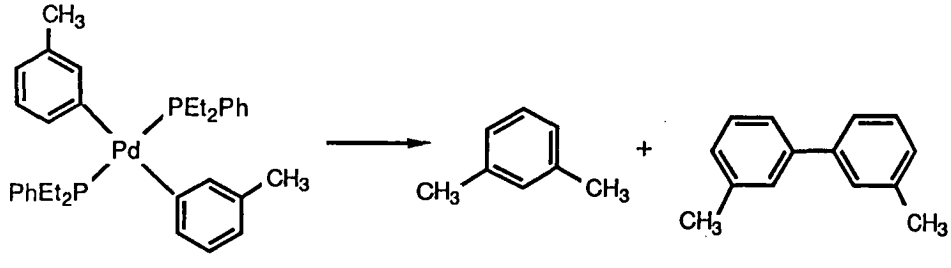
The rapid rate of reductive elimination involving the palladium(IV) intermediate provides an explanation for the observation that the rates of reductive elimination from palladium(II) complexes are often slower than the rates of any of the individual steps in the catalytic coupling reactions of organohalides with organometals, *e.g.* Moravskiy and Stille[20e] found a 400 fold increase in the rate of reduction elimination of ethane from $\{PdMe_2(PMePh_2)_2\}$ in the presence of MeI, *i.e. via* **Pd(IV)**, compared with elimination of ethane directly from $\{PdMe_2(PMePh_2)_2\}$, *i.e. via* Pd(II).

Similarly, Kurosawa *et. al.*[68] have recently reported that addition of allylic electrophiles, *e.g.* methallylchloride, greatly accelerated the rate of reductive elimination from η^3-alkyl(aryl)palladium(II) complexes, and, significantly, the allylic substrate was incorporated in the products, *e.g.* equation 5.2.2-22. A reaction mechanism featuring a palladium(IV) intermediate (of unknown structure) was proposed.[68]



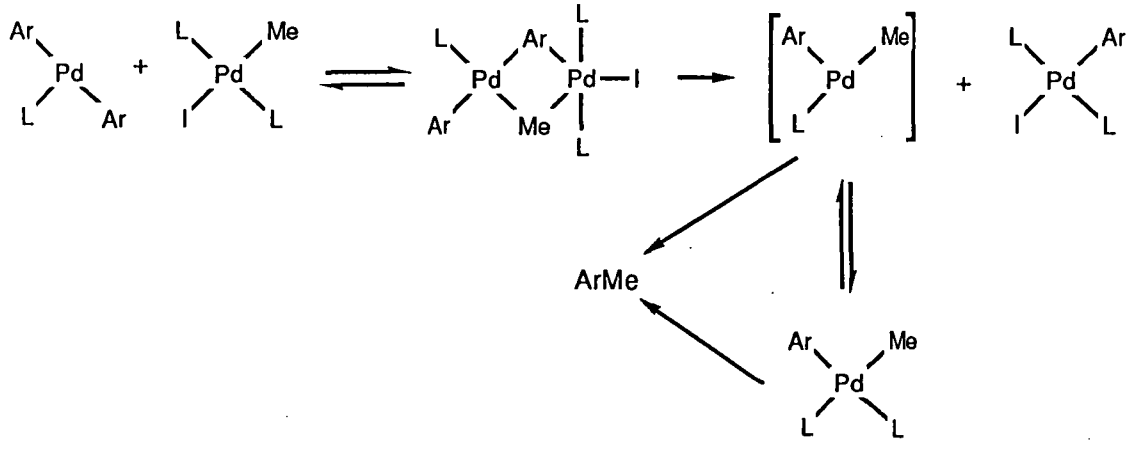
5.2.2-22

In contrast to this, however, Ozawa *et. al.*[69a] have reported that reaction of $\{PdR_2(L_2)\}$ (R=*m*-tolyl; L=PEt_2Ph) with MeI, to produce *m*-xylene together with 3-3'-bitolyl, equation 5.2.2-23, proceeds *via* an intermolecular process between $\{PdR_2(L_2)\}$ and $\{PdMeI(L_2)\}$ (scheme 5.2.2-7), and not *via* a palladium(IV) intermediate. In a later paper[69b] Ozawa *et. al.* found that an analogous mechanism was also operating for the production of biaryls from $\{PdR_2(L_2)\}$ (R=*m*-tolyl, phenyl; L=PEt_2Ph) and aryliodides.[69b]



5.2.2-23

Scheme 5.2.2-7



5.3 ALKYLPALLADIUM(IV) COMPLEXES WITH BIDENTATE LIGANDS

Irrespective of the catalytic cycle followed for the cross-coupling reaction scheme 5.2.2-4 or scheme 5.2.2-6 , the intermediates $\{Pd^{II}R_2(L_2)\}$ and $\{Pd^{II}RX(L_2)\}$ are involved. Further, $\{Pd^{II}RX(L_2)\}$ is formed from an interaction of the organohalide with $\{Pd^{II}R_2(L_2)\}$, either *via* a palladium(IV) intermediate, equation 5.3-1, or *via* a palladium(0) intermediate equation 5.3-2.

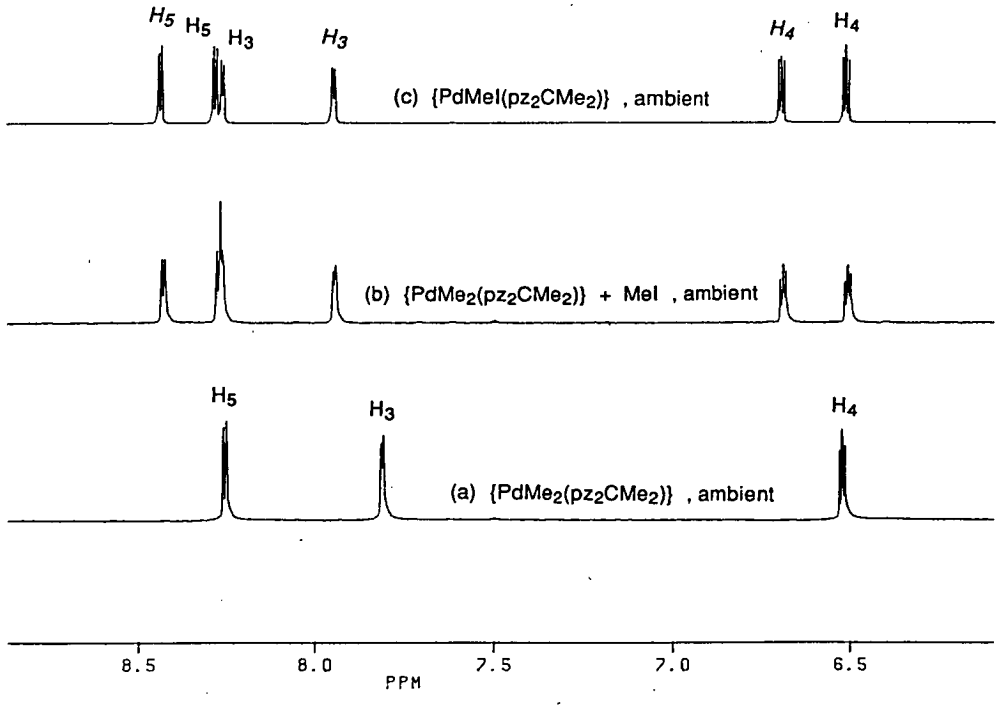
$$\{Pd^{II}R_2(L_2)\} \xrightarrow{RX} \{Pd^{IV}R_3X(L_2)\} \rightarrow \{Pd^{II}RX(L_2)\} + R\text{-}R \qquad 5.3\text{-}1$$

$$\{Pd^{II}R_2(L_2)\} \rightarrow \{Pd^{0}(L_2)\} \xrightarrow[+R\text{-}R]{RX} \{Pd^{II}RX(L_2)\} \qquad 5.3\text{-}2$$

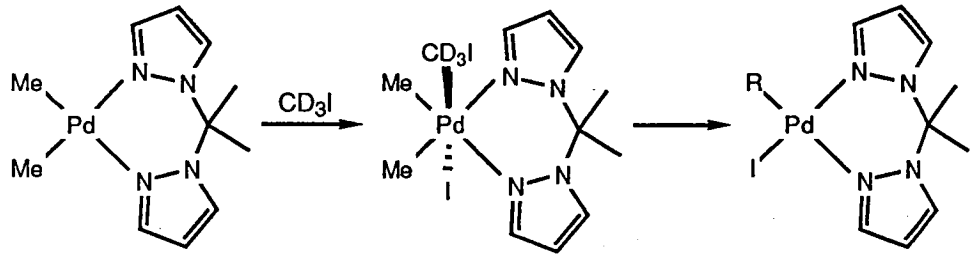
To study the interaction of a diorganopalladium(II) substrate with an organohalide to produce the corresponding monoorganohalopalladium(II) complex, the reaction of $\{PdMe_2(pz_2CMe_2)\}$ (I) with methyliodide was initially investigated. It was found that upon addition of MeI to an acetone solution of (I) at ambient temperature a gas was evolved and the initially clear colourless solution became yellow immediately. Evaporation of the acetone solvent gave $\{PdMeI(pz_2CMe_2)\}$ (II), identified from its N.M.R. spectrum compared with a spectrum of an authentic sample.

The experiment was repeated (figure 5.3-1) by sealing a sample of (I) (in acetone-D6) in an N.M.R. tube equipped with a septum, with MeI added *via* a microlitre syringe, and the results of this *in situ* reaction also revealed the formation of ethane as a product. The Pd-Me region of the product spectrum displayed two resonances at 0.83 ppm and 0.82 ppm, and purging this solution with N_2 resulted in the disappearance of the peak at 0.83 ppm, but no change in all other resonances. Thus, the resonance at 0.83 ppm is assigned as ethane, and an authentic sample of ethane in acetone-D6 was found to give a resonance at 0.83 ppm. Further support for this assignment was obtained upon repeating the *in situ* reaction described above on a larger scale, and analysing the gas evolved by g.c./m.s., revealing ethane as the only gas present.

Figure 5.3-1. ^{1}H NMR of {$PdMe_2(pz_2CMe_2)$} + MeI in Acetone-D6.



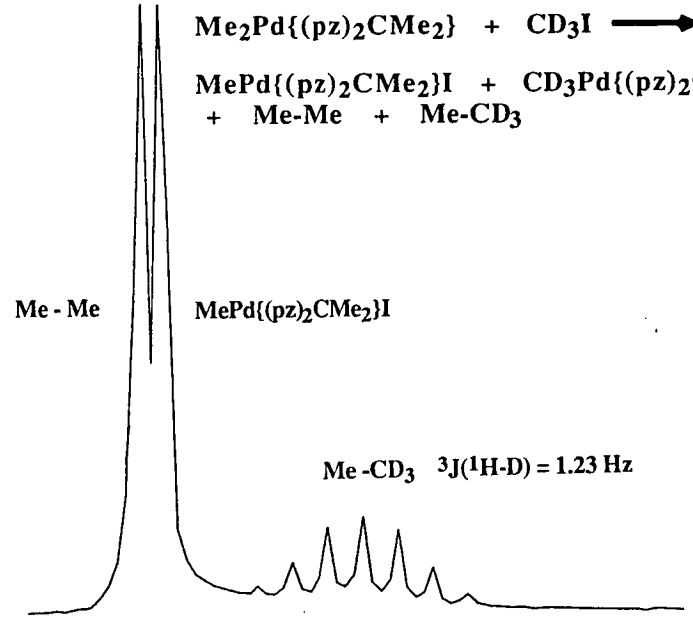
Evidence for the involvement of a palladium(IV) intermediate was obtained from an *in situ* reaction of CD_3I with (I) to produce both CH_3CH_3 and CH_3CD_3 in *ca.* 1:1 ratio (N.M.R. identification), figure 5.3-2. Thus, reaction according to equation 5.3-3 is proposed.



5.3-3

+ MeMe + $MeCD_3$

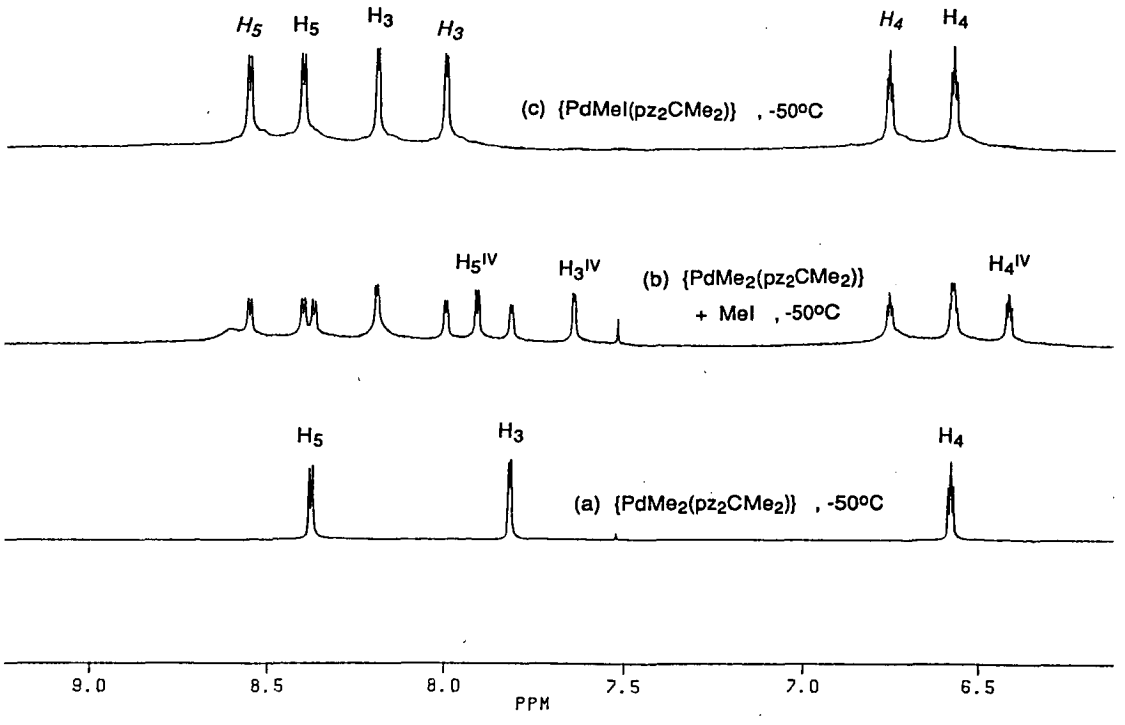
(R=Me, CD_3)



In an attempt to detect the proposed Pd(IV) intermediate, an *in situ* reaction between (I) and MeI was performed at low temperature, and at -50°C a spectrum displaying aromatic resonances for both (I) and (II) was observed, together with a third species containing pz_2CMe_2, figure 5.3-3b. The resonances arising from (I) and (II) are clearly differentiated upon comparison of figures 5.3-3a and c with figure 5.3-3b, and the third species has been assigned as $\{PdMe_3I(pz_2CMe_2)\}$. Consistent with the assignment of $\{PdMe_3I(pz_2CMe_2)\}$ as an intermediate, its resonances decrease with time as those for (II) increase. Unfortunately, while aromatic resonances for $\{Pd^{IV}Me_3I(pz_2CMe_2)\}$ can be clearly discerned, definitive assignment of the Pd^{IV}-Me

resonances and C-Me bridgehead resonances is not possible, owing to the complexity and broadness of resonances in the aliphatic region at the low reaction temperature required for stability of the palladium(IV) product.

Figure 5.3-3. ^{1}H NMR of {$PdMe_2(pz_2CMe_2)$} + MeI in Acetone-D6 at -50°C.



Construction of molecular models indicates that for {$PdMe_3I(pz_2CMe_2)$} acute steric interaction is expected between an axial bridgehead methyl-group and either the axial Pd-Me or Pd-I groups of octahedral Pd(IV). Thus, the relief of steric interactions may be one of the factors influencing the rate of reductive elimination. To overcome this possible effect, oxidative addition reactions of MeI with the complex {$PdMe_2(bipy)$}, containing the 'planar' ligand bipy (2,2'-bipyridyl), were investigated. Platinum(II) complexes with ligands such as bipy and phen (1,10-phenanthroline) are known to be particularly reactive towards oxidative addition.[70]

5.3.1 Isolated Alkylpalladium(IV) Complexes

5.3.1-i Oxidative Addition to {$PdMe_2$(bipy)}

(a) Preliminary Studies

An *in situ* reaction at ambient temperature between {$PdMe_2$(bipy)} (I) and MeI **immediately** gave a spectrum (II) with all resonances downfield from those for (I), figure 5.3.1-1. Resonances for (II) slowly decreased, with a concomitant increase in resonances for {PdMeI(bipy)} (III) and the appearance of ethane, which could be removed upon purging the solution with N_2. Based on this behaviour, (II) is assigned as {$PdMe_3I$(bipy)}, and as only one pyridine ring environment is observed, and two Pd^{IV}-Me peaks in 2:1 ratio, the structure shown in figure 5.3.1-2 is assigned to (II).

Figure 5.3.1-1. ^{1}H NMR of {$PdMe_2$(bipy)} + MeI in Acetone-D6

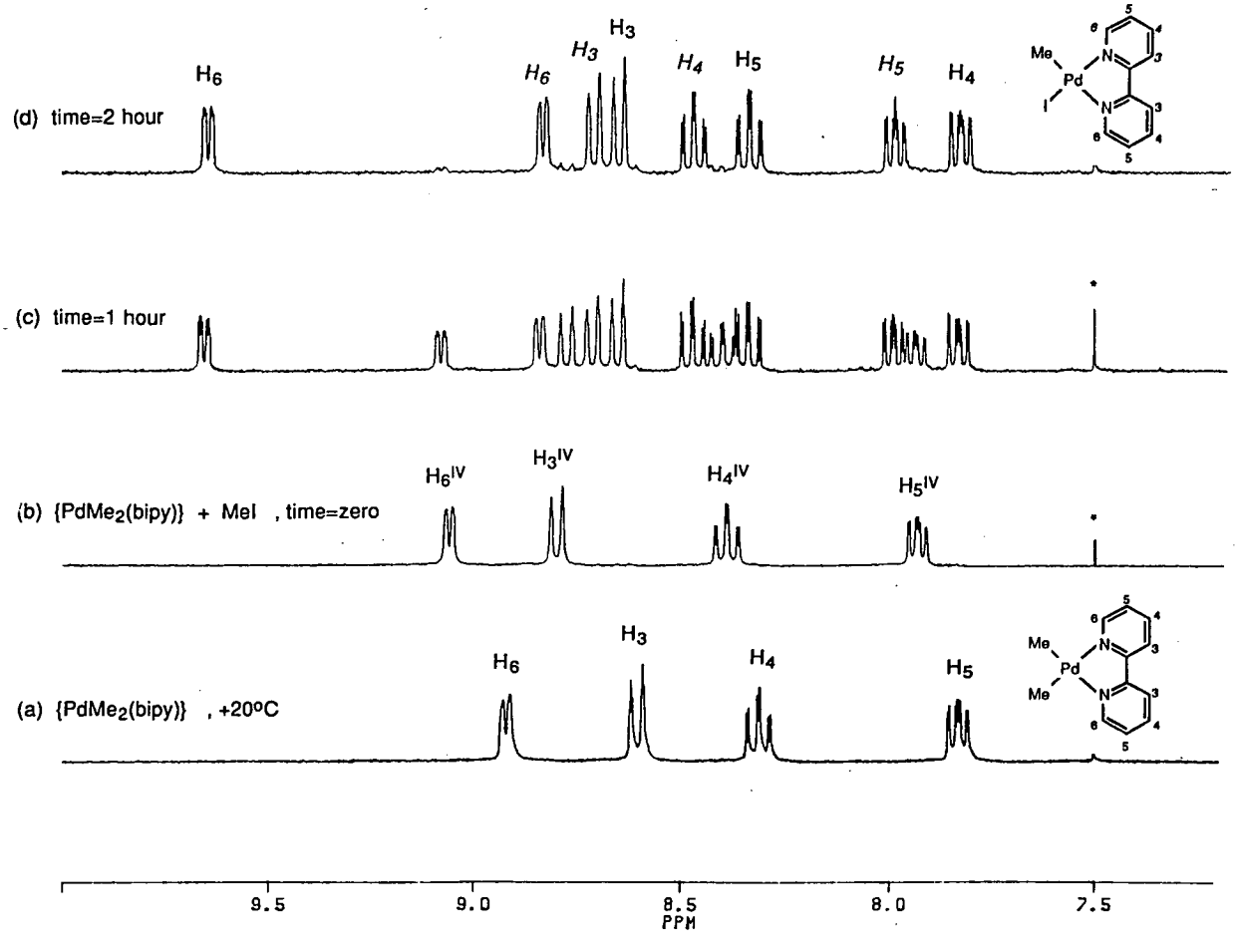
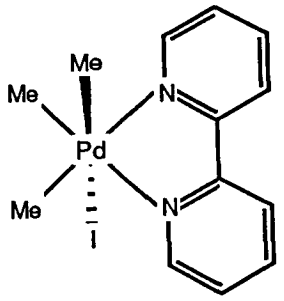
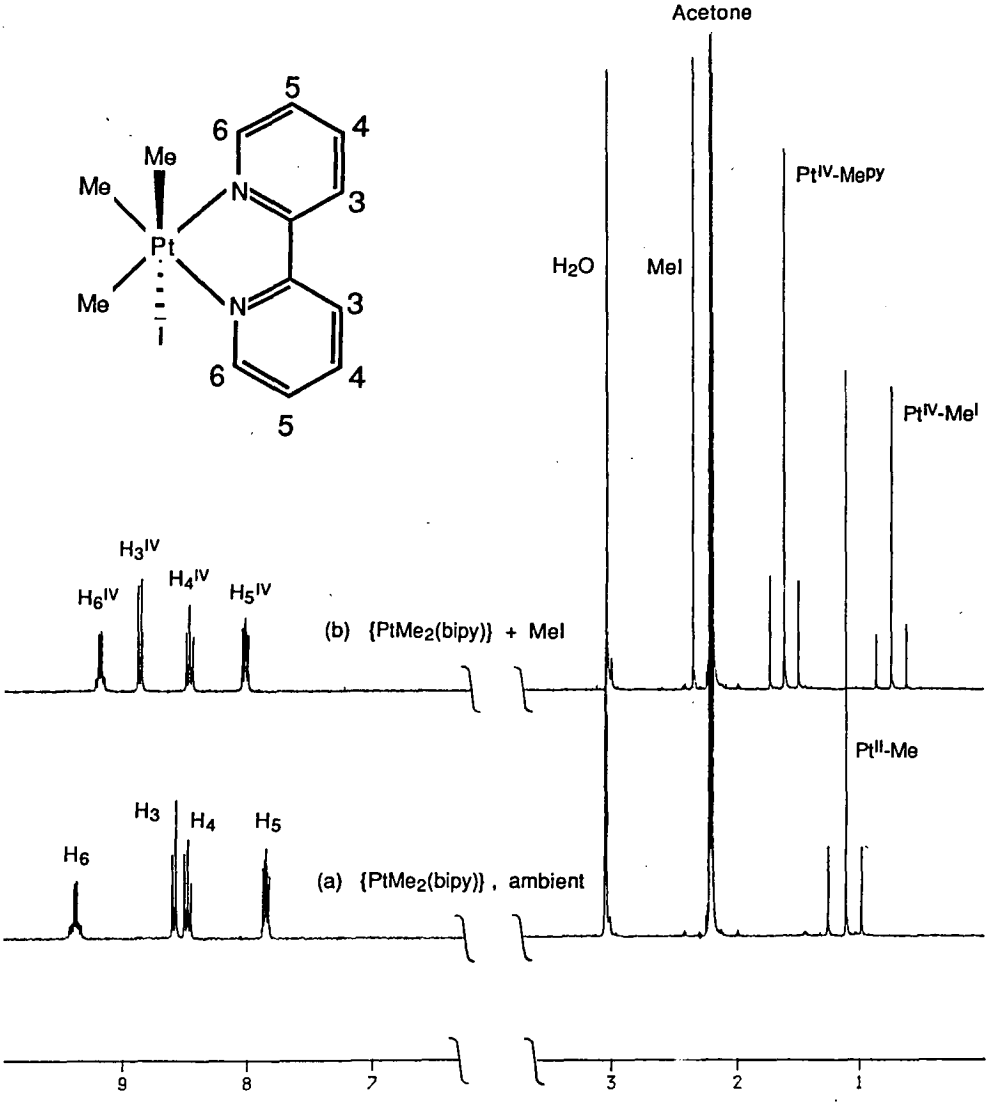


Figure 5.3.1-2.



Spectra for the closely related platinum analogues {$PtMe_2(bipy)$} and {$PtMe_3I(bipy)$}, prepared from {$PtMe_2(bipy)$} by an identical *in situ* reaction, are displayed in figure 5.3.1-3, and it is interesting to note that for both palladium and platinum a shift to lower field occurs on progressing from M^{II}-Me (*trans* to bipy) to M^{IV}-Me (*trans* to bipy).

Figure 5.3.1-3. ^1H NMR of {$PtMe_2(bipy)$} + MeI in Acetone-D6.

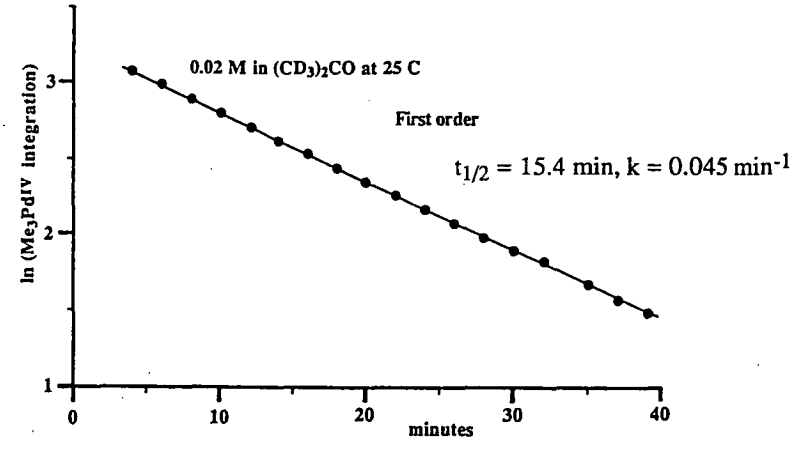


While 1,1-reductive elimination has been reported to obey 1st order kinetics for both Pt(IV)[71] and Pd(II),[20d,e] kinetics for reductive elimination from Pd(IV) have not been reported. Hence, a preliminary kinetic study of the reductive elimination of ethane from {$PdMe_3I(bipy)$} was undertaken, and the reaction was followed by monitoring the rate of disappearance of the Pd^{IV}-Me resonances with time; absolute integration values for Pd^{IV}-Me were obtained by comparison with TMS as an internal standard. From a process of trial and error 0.02M acetone solutions of (II) were found to be suitable and, due to the insolubility of isolated (II) in acetone, were formed as required from an *in situ* reaction, and reaction temperatures of 25°C were found to give convenient experimental times.

Figure 5.3.1-4 displays a plot of ln(Pd^{IV}-Me integration) versus time, and clearly illustrates that the reductive elimination of ethane from {$PdMe_3I(bipy)$} follows good 1st order kinetics (correlation coefficient=0.9997), with a rate constant of 0.045 min^{-1} and $T_{1/2}$ of 15.4 minutes.

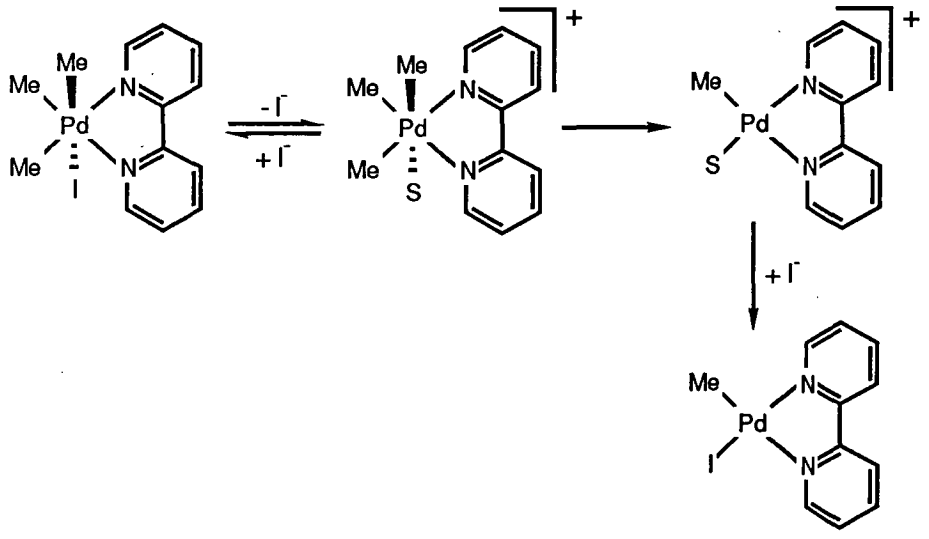
Figure 5.3.1-4.

$$Me_3Pd^{IV}(bipy)I \longrightarrow MePd^{II}(bipy)I + Me\text{-}Me$$



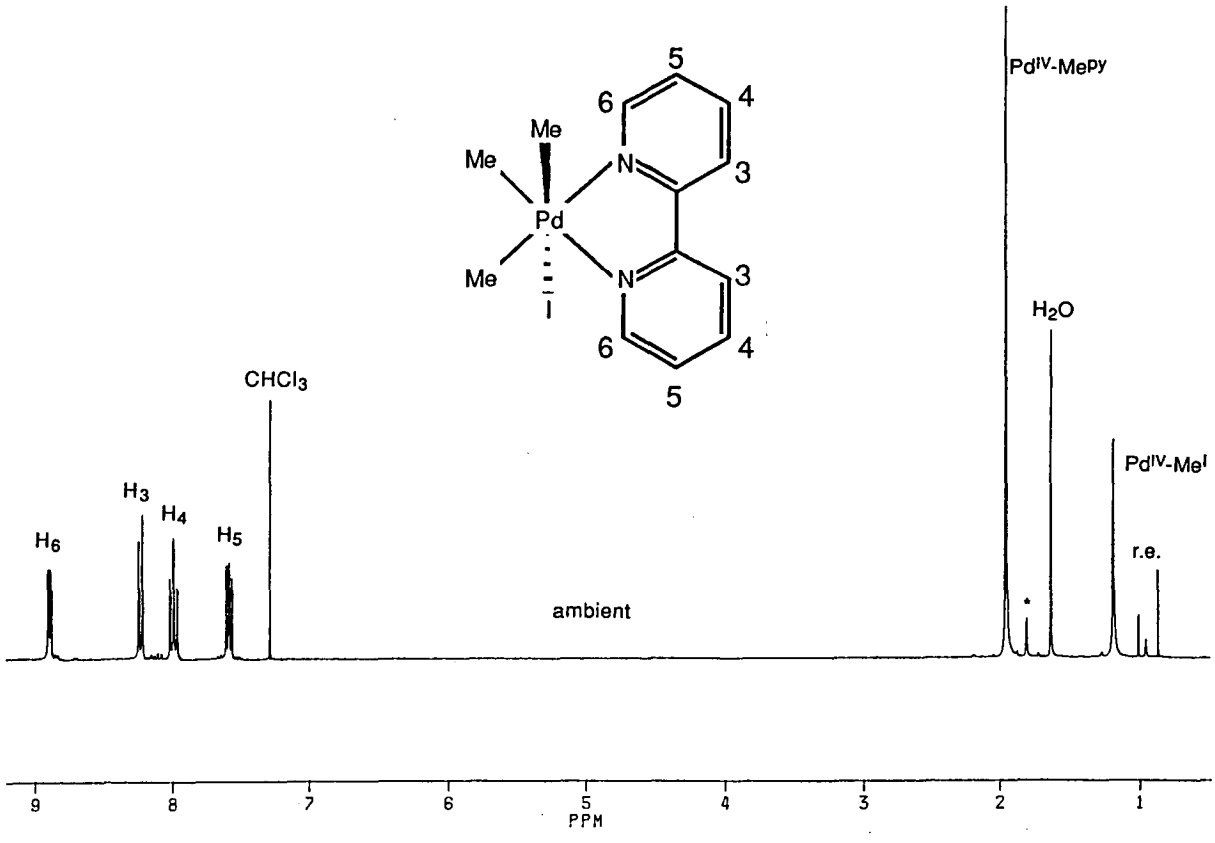
Similar reactions with the addition of D_2O, to increase the solvent polarity, or the addition of KI, to provide an excess of iodide in solution, also obeyed 1st order kinetics, but in the former an increase in rate was observed, while in the latter a decrease was observed. Based on this behaviour the mechanism depicted in equation

5.3.1-1 is proposed, involving dissociation of iodide **prior** to reductive elimination of ethane. A similar mechanism has been proposed by Ettorre[72] for the reductive elimination of PhI from $\{PtPh_2I_2(PEt_3)_2\}$ to form *trans*-$\{PtPhI(PEt_3)_2\}$



The reaction also obeyed 1st order kinetics at 0°C, but the rate constant was diminished to 0.0011 min^{-1}, giving $T_{1/2}$ of 620 minutes and thus preparation and isolation of $\{PdMe_3I(bipy)\}$ was considered possible if the oxidative addition reaction and work-up is performed at, or below, 0°C. Indeed, addition of MeI to a saturated acetone solution of $\{PdMe_2(bipy)\}$ at 0°C resulted in immediate discharge of solution colour, and slow (*ca.* 15 min) evaporation to *ca.* 1/2 volume at 0°C by rotary evaporation afforded a white highly crystalline solid. This solid displayed poor solubility in acetone-D6, but an N.M.R. spectrum could be readily obtained in chloroform-D, figure 5.3.1-5, and is identical to that obtained from an *in situ* reaction in acetone-D6. The reductive elimination of ethane in chloroform-D also obeyed 1st order kinetics, but at 25°C the elimination of ethane was slower than under identical conditions in acetone, with $T_{1/2}$ of 45 minutes. A correct microanalysis for $\{PdMe_3I(bipy)\}$ was obtained, and the structure of $\{PdMe_3I(bipy)\}$ was determined using X-ray crystallography. Thermolysis of $\{PdMe_3I(bipy)\}$ at 110°C produced $\{PdMeI(bipy)\}$ prior to general decomposition to palladium metal at *ca.* 200°C.

Figure 5.3.1-5. ^1H NMR of {$PdMe_2$(bipy)} in Chloroform-D.



(b) Structure Determination of {$PdMe_3I$(bipy)}

Crystals of the complex {$PdMe_3I$(bipy)} suitable for a structural study were obtained directly from a reaction between MeI and {$PdMe_2$(bipy)} under the conditions described above. The structure was determined by Dr. A. H. White and colleagues of the University of Western Australia, and is displayed in figure 5.3.1-6; selected bond lengths and angles are given in table 5.3.1-1.

Palladium exhibits an octahedral geometry but with distortion resulting from the 'bite' of bipy, giving a N-Pd-N angle of 75.6(2)°. The C-Pd-C angles are also less than 90° with C(a)-Pd-C(b) being the smallest (86.6(3)°), perhaps resulting from steric interactions C(a)····H_6^b and C(b)····H_6^a. The bipy ligand skeleton is substantially planar, and with deviation of Pd, C(a), C(b) from the bipy mean plane of 0.218, 0.496 and 0.556 Å respectively.

Table 5.3.1-1. Coordination Geometry for the Palladium Atom in *fac*-{$PdMe_3I(bipy)$}; Distances in Å Angles in °.

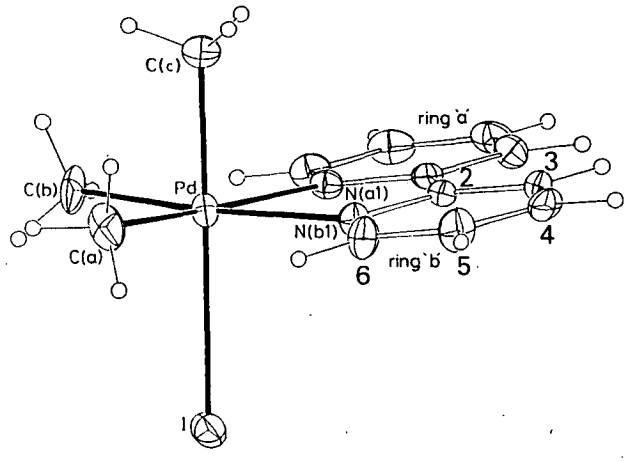
Bond Distances			
Pd-C(a)	2.046(7)	Pd-N(a1)	2.188(5)
Pd-C(b)	2.034(7)	Pd-N(b1)	2.173(5)
Pd-C(c)	2.040(6)	Pd-I	2.834(1)
Bond Angles			
C(a)-Pd-C(b)	86.3(3)	C(c)-Pd-N(b1)	89.3(3)
C(a)-Pd-C(c)	87.0(3)	C(c)-Pd-I	178.1(2)
C(b)-Pd-C(c)	86.8(3)	N(a1)-Pd-N(b1)	75.6(2)
C(a)-Pd-N(a1)	172.3(3)	N(a1)-Pd-I	89.8(1)
C(a)-Pd-N(b1)	97.4(3)	N(b1)-Pd-I	92.1(1)
C(a)-Pd-I	93.9(2)	Pd-N(a1)-C(a2)	115.5(4)
C(b)-Pd-N(a1)	100.1(3)	Pd-N(a1)-C(a6)	126.3(4)
C(b)-Pd-N(b1)	174.2(3)	Pd-N(b1)-C)b2)	116.1(4)
C(b)-Pd-I	91.7(2)	Pd-N(b1)-C(b6)	125.3(4)
C(c)-Pd-N(a1)	89.5(2)	N(a1)-C(a2)-C(b2)	116.4(5)
		N(b1)-C(b2)-C(a2)	115.6(6)

The bipy ligand skeleton is substantially planar (χ^2=70), with an interplanar angle of 2.1° between rings a and b, and with deviations of Pd, C(a), C(b) from the mean plane of bipy being 0.218, 0.556, 0.496 Å respectively, *i.e.* Pd lies will above the C_2N_2 plane and towards I.

Palladium(IV) complexes are not numerous, and thus structural determinations of Pd(IV) complexes are rare, and further, are represented only for inorganic derivatives. The most directly comparable Pt(IV) complex is *fac*-{$PtMe_3I((3,5\text{-}Me_2\text{-}pz)_2CH_2)$} which has a similar '$MC_3IN_2$' donor set with the iodo-ligand *trans* to a methyl group.[73] Both Pd^{IV}-I (2.834(1)Å) and Pd^{IV}-C (2.034(7)-2.046(7)Å) compare favourably to that found for Pt^{IV}-I (2.843(1)Å) and Pt^{IV}-C (2.032(5)-2.077(6)Å). The Pd^{IV}-N (2.173(5)-2.188(5)Å) distances are shorter than that found for Pt^{IV}-N

(2.236(4)Å), but they are longer than that found for Pd^{IV}-N in {$PdCl_4$(bipy)} (2.037(4)-2.044(4)Å),[3a] although this may be related to the higher *trans* effect of the methyl group.

Figure 5.3.1-6.

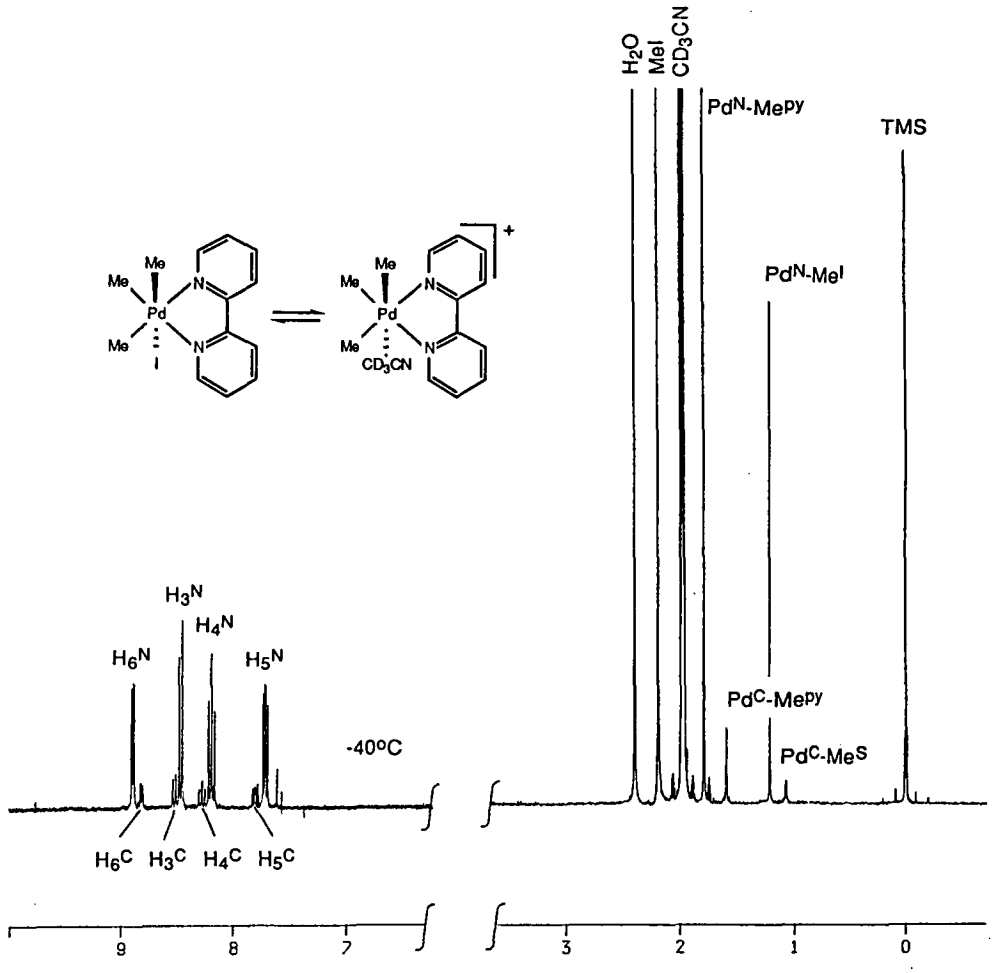


(c) N.M.R. Studies in Acetonitrile-D3

Addition of MeI to {$PdMe_2$(bipy)} in acetonitrile-D3 at -40°C immediately produced two products in 3:1 ratio, figure 5.3.1-7. Methyl-Pd^{IV} resonances due to the major product {$PdMe_3I$(bipy)} were at 1.79 ppm (Pd^{IV}-Me *trans* to bipy) and 1.20 ppm (Pd^{IV}-Me *trans* to I), while the minor product was assigned to the ionic [$PdMe_3(CD_3CN)$(bipy)]I with 1.61 ppm (Pd^{IV}-Me *trans* to bipy) and 1.06 ppm (Pd^{IV}-Me *trans* to CD_3CN).

On warming, methyl group resonances for the cation broadened, with coalescence ≥-5°C, but bipy resonances for the cation and all resonances for {$PdMe_3I$(bipy)} remained sharp, consistent with intramolecular scrambling of methyl environments in the cation. At higher temperatures (> -15°C) bipy resonances for the neutral and cationic complexes were coalesced, and the bipy and methyl resonances were broad compared to the sharp, growing resonances for {PdMeI(bipy)} indicating exchange between [$PdMe_3(CD_3CN)$(bipy)]I and {$PdMe_3I$(bipy)}. Both the processes described above were reversible, *i.e.* upon re-cooling, and similar results were found upon dissolution of {$PdMe_3I$(bipy)} in acetonitrile-D3.

Figure 5.3.1-7. ^{1}H NMR of {$PdMe_2$(bipy)} + MeI in Acetonitrile-D3 at -40°C.



From these results in acetonitrile-D3, it is most likely that scrambling occurs *via* a transient cation, *e.g.* from N.M.R. studies in acetone where it was found that addition of CD_3I to {$PdMe_2$(bipy)} at -60°C produced a spectrum exhibiting two Pd^{IV}-Me resonances in 2:1 ratio, indicating scrambling of CD_3 and CH_3 had already occurred.

(d) Kinetic Studies, and an Estimate of the Pd^{IV}-C Bond Energy

The kinetics of the oxidative addition of MeI to {$PdMe_2$(bipy)} and the reductive elimination of ethane from {$PdMe_3I$(bipy)}, together with an estimate of the Pd^{IV}-carbon bond energy, have been determined by Prof. R. J. Puddephatt and colleagues at the University of Western Ontario, London, Canada, using samples of {$PdMe_2$(bipy)} and {$PdMe_3I$(bipy)} supplied from our laboratory. The results for

palladium are compared with results from an analogous study with platinum, and the discussion that follows represents a summary of their work.[74]

Oxidative Addition of Methyliodide

The kinetics of the oxidative addition in acetone solution, using at least an 8-fold excess of MeI, were monitored by UV-visible spectrophotometry. Good first order kinetics were followed and the observed first order rate constants were directly proportional to the concentration of MeI, thus overall second order kinetics were followed, first order in each reagent.

For comparison, the oxidative addition to {$PtMe_2$(bipy)} was also studied and the activation parameters for both reactions were determined. The second order rate constants for reaction of MeI with {$PdMe_2$(bipy)} and {$PtMe_2$(bipy)} at 20°C were 3.23±0.08 and 40.0±0.1 $lmol^{-1}s^{-1}$ respectively, and the corresponding activation parameters were E_a=25.3±0.6 and 24.94±0.06 $kJmol^{-1}$ and ΔS‡(20°C)=-148±2 and -129.0±0.2 $JK^{-1}mol^{-1}$. The platinum complex reacts over ten times as fast as the palladium analogue, largely due to a less unfavourable ΔS‡ term.

All of the kinetic data, especially the large negative ΔS‡ values, strongly support the S_N2 mechanism of oxidative addition in both cases. Indeed in a separate study, the low temperature reaction of {$PtMe_2$(bipy)} with MeI in acetonitrile-D3 was found to give the ionic intermediate [$PtMe_3(CD_3CN)$(bipy)]I which subsequently decays to {$PtMe_3I$(bipy)}, thus providing good evidence for the S_N2 mechanism of oxidative addition.[56b]

Reductive Elimination of Ethane

The reductive elimination of ethane from {$PdMe_3I$(bipy)} was also monitored by UV-visible spectrophotometry, using the increase in absorbance of 380 nm due to the product {PdMeI(bipy)}. The majority of the work was performed in acetone, in which the reductive elimination followed first order kinetics. The observed rate constant at 20°C was only slightly decreased by the presence of an excess of MeI or bipy, but in the presence of an excess of NaI the rate was dramatically reduced. This

result strongly indicates that reductive elimination occurs from the cation $[PdMe_3(bipy)]^+$. A detailed study of the rate of reductive elimination as a function of iodide concentration was consistent with the kinetic scheme outlined below, scheme 5.3.1-1, and leads to the kinetic expression in equation 5.3.1-2, and the observed first order rate constant in equation 5.3.1-3.

Scheme 5.3.1-1.

$$[PdMe_3I(bipy)] \rightarrow [PdMeI(bipy)] + C_2H_6 \quad (1)$$

$$[PdMe_3I(bipy)] \leftrightarrow [PdMe_3(bipy)]^+ + I^- \quad (2)$$

$$[PdMe_3(bipy)]^+ \rightarrow [PdMe(bipy)]^+ + C_2H_6 \quad (3)$$

$$[PdMe(bipy)]^+ + I^- \rightarrow [PdMeI(bipy)] \quad (4)$$

$$-\frac{\delta [2]}{\delta T} = K_1 + \frac{K_2K_4 [2]}{(K_3 [I^-] + K_4)} \qquad 5.3.1\text{-}2$$

$$K_{obs} = K_1 + \frac{K_2K_4}{(K_3 [I^-] + K_4)} \qquad 5.3.1\text{-}3$$

Consistent with this mechanism is the observation that the rate of reductive elimination in various solvents follows the order of increasing solvent polarity benzene < acetone < methanol. The activation parameters for the reaction in acetone, E_a=65± 13 kJmol^{-1} and $\Delta S\ddagger$(20°C)=-66± 34 JK^{-1} mol^{-1}, also suggest the formation of a polar intermediate. The limiting rate of reaction in methanol in the presence of a large excess of iodide was 13 times greater than that in acetone under identical reaction conditions, suggesting that for reaction 1 in scheme 5.3.1-1 a polar intermediate or transition state may be involved. The activation parameters for the reaction in the presence of an excess of iodide were determined in acetone, Ea=78± 11 kJmol^{-1} and $\Delta S\ddagger$(20°C)=-53±25 JK^{-1}mol^{-1}, and methanol, E_a=39± 5 kJmol^{-1} and $\Delta S\ddagger$(20°C)=-164± 17 JK^{-1}mol^{-}

^{1}, and again suggest a polar intermediate or transition state. A likely explanation for these data is that at least partial ionisation of iodide occurs before reductive elimination. Thus, the precursor state to reductive elimination could be a polar species $[PdMe_3(bipy)^{\delta+}\cdots I^{\delta-}]$ or a tight ion pair $[PdMe_3(bipy)]I$, and in neither case would inhibition by iodide occur, but both species are highly polar and would cause the solvent ordering required by the negative $\Delta S\ddagger$ values.

The complex $\{PtMe_3I(bipy)\}$ is very stable and decomposes only at *ca.* 270°C to give methane as the major product. Hence, it is not possible to compare the mechanisms in this case.

The Palladium-Carbon Bond Energy

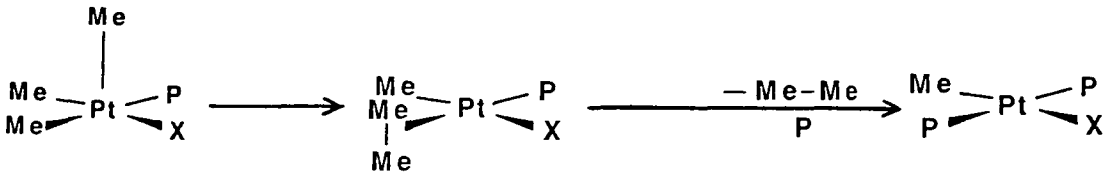
Monitoring of the reductive elimination of ethane from $\{PdMe_3I(bipy)\}$ to give $\{PdMeI(bipy)\}$ was accomplished by differential scanning calorimetry (DSC), and a clean exotherm commencing at *ca.* 80°C and finishing at *ca.* 120°C was obtained. Weight loss was expected to be 6.9% and found to be 7.3±0.2% and the product was confirmed to be pure $\{PdMeI(bipy)\}$ by N.M.R. The integrated area of the exotherm centred at *ca.* 110°C gave ΔH=-105±2 kJmol^{-1}, and assuming this enthalpy change corresponds to formation of the C-C bond of ethane (368 kJmol^{-1}) and loss of two Pd-Me bonds, D(PdMe)=131.5±6 kJmol^{-1}. Thus, the Pd-C bonds are reasonably strong, and may be compared with $\{PtMe_3I(PMe_2Ph)_2\}$ where a value of D(PtMe)=144 kJmol^{-1} was determined by DSC for a similar reduction elimination reaction.[71] A comparison of D(PtMe) for $\{PtMe_3I(bipy)\}$ was not possible due to the complexity of its decomposition.

Both the oxidative addition of MeI and reductive elimination of ethane appear to involve the intermediacy of the solvated cation $[PdMe_3(bipy)]^+$, at least to a major extent in solution reactions. The rates of reaction and the activation parameters for oxidative addition of MeI to $\{PdMe_2(bipy)\}$ and $\{PdMe_2(bipy)\}$ are similar, and the mechanisms are clearly the same, namely the S_N2 mechanism.

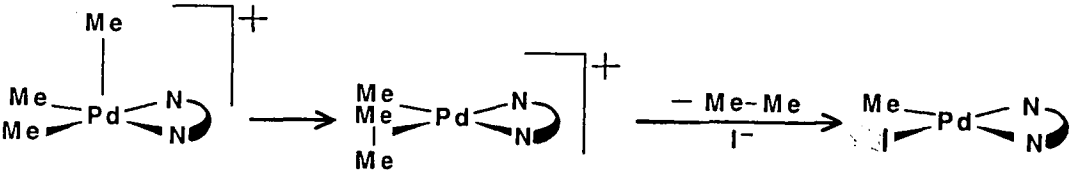
The kinetics of the reductive elimination of ethane from $\{PdMe_3I(bipy)\}$ are consistent with a concerted elimination of ethane, and in support of this the apparent

activation energy Ea for reductive elimination in acetone or methanol is much lower than the estimated Pd-Me bond energy. Thus, the reductive elimination may occur in a similar way to that proposed earlier for the elimination of ethane from $\{PtMe_3I(PMe_2Ph)_2\}$,[71] equations 5.3.1-4,5.

$$Me_3Pt(PR_3)_2X \longrightarrow \textit{trans}\text{-}MePt(PR_3)_2X + Me\text{-}Me$$



$$Me_3Pd(bipy)I \longrightarrow \textit{cis}\text{-}MePd(bipy)I + Me\text{-}Me$$

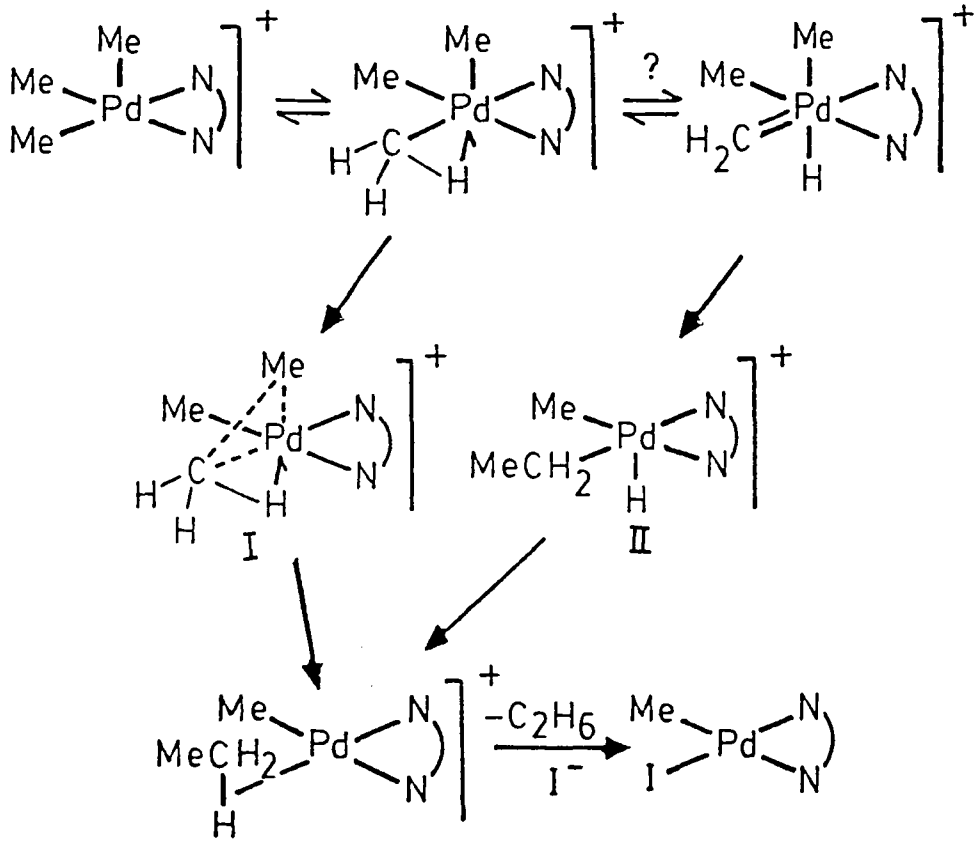


However, an alternative mechanism is possible in view of more recent evidence that α-elimination can occur readily and reversibly,[75] and this mechanism, scheme 5.3.1-2, accounts in a rational manner for the requirement of a vacant coordination site prior to reductive elimination. Intermediate (I) is favoured over (II), since the latter could reductively eliminate methane, ethane or β-eliminate ethene, and so would not be expected to give the high observed selectivity for formation of ethane.

(e) Reaction with Benzylbromide

To investigate the ability of $\{PdMe_2(bipy)\}$ to undergo oxidative addition of other organohalides, *in situ* reactions between $\{PdMe_2(bipy)\}$ and ethyliodide, *n*-propyliodide, allylbromide, neopentylchloride, phenyliodide and benzylbromide were studied. Only benzylbromide gave a stable oxidative addition product in acetone-D6 at ambient temperature. Indeed, this product displayed much higher stability than $\{PdMe_3I(bipy)\}$.

Scheme 5.3.1-2.



Based on the observed stability of the benzylbromide addition product a preparative scale reaction was attempted with reaction conditions identical to those employed for the preparation of {$PdMe_3I(bipy)$}, affording a white crystalline solid. This solid analysed correctly for {$PdMe_2(CH_2Ph)Br(bipy)$} and an N.M.R. spectrum in chloroform-D (figure 5.3.1-8) confirmed the formation of a palladium(IV) complex from the downfield position of the Pd^{IV}-Me resonances, and the presence of one pyridine ring environment and identical benzylic-CH_2-protons indicating a *trans* oxidative addition, figure 5.3.1-9. The benzene ring of the benzyl group is proposed to lie above the bipy ligand, with this orientation suggested by the upfield shift of the aromatic benzyl protons compared with the free organohalide.

The stability of {$PdMe_2(CH_2Ph)Br(bipy)$} is appreciably greater than {$PdMe_3I(bipy)$}, *e.g.* heating an acetone solution at 50°C for 15 minutes is necessary to give the palladium(II) product and the palladium(IV) reactant in similar quantities, but {$PdMe_3I(bipy)$} is fully decomposed to {PdMeI(bipy)} and ethane after *ca.* 10

minutes at 40°C. The reductive elimination of {$PdMe_2(CH_2Ph)Br(bipy)$} produces ethane only, with no trace of ethyl benzene or {PdMeBr(bipy)} evident, and the palladium(II) product formed contains a benzyl group with integration as expected for {$Pd(CH_2Ph)Br(bipy)$}.

Figure 5.3.1-8. ^1H NMR of {$PdMe_2(CH_2Ph)Br(bipy)$} in Chloroform-D.

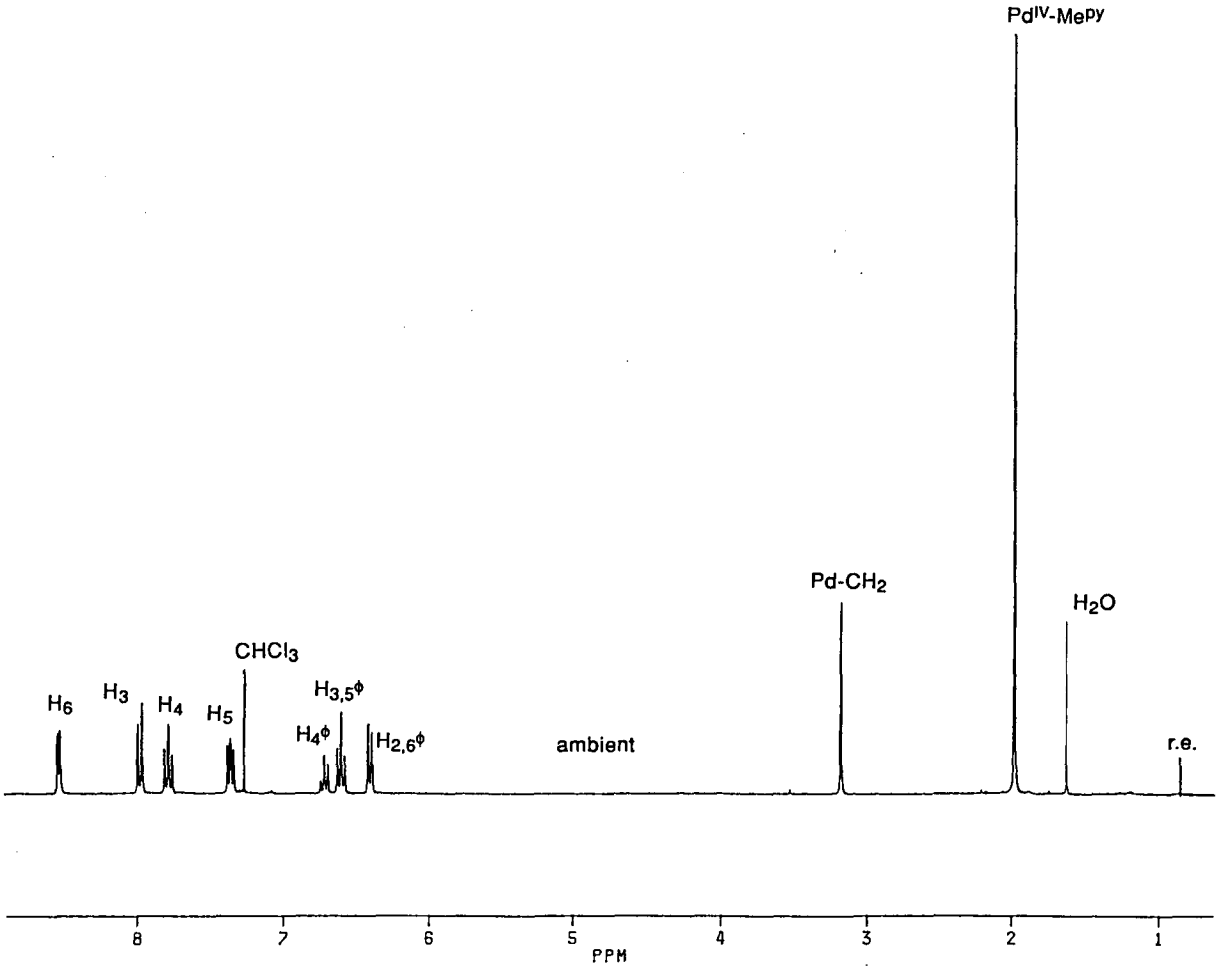
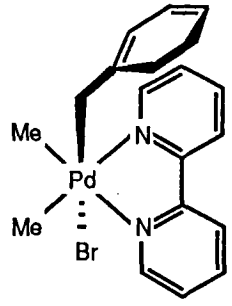


Figure 5.3.1-9.



5.3.1-ii Oxidative Addition to {$PdMe_2$(phen)}

An *in situ* reaction between {$PdMe_2$(phen)} and MeI in acetonitrile-D3 at -40°C immediately produced a spectrum displaying the presence of the neutral (Pd^{IV}-Me:1.79 ppm *trans* to phen, 1.12 ppm *trans* to I) and cationic (Pd^{IV}-Me:1.59 ppm *trans* to phen, 0.99 ppm *trans* to CD_3CN) complexes {$PdMe_3I$(phen)} and [$PdMe_3(CD_3CN)$(phen)]I in *ca.* 5:2 ratio respectively. On warming, similar behaviour was observed to that already described for an analogous reaction with {$PdMe_2$(bipy)}.

Repeating this reaction at -60°C in acetone-D6 also produced the palladium(IV) complex {$PdMe_3I$(phen)} readily, and the reaction appeared to occur at a comparable rate to that found for {$PdMe_2$(bipy)}. The solution remained unchanged upon warming to 0°C, although further warming to 20°C resulted in slow reductive elimination of ethane. The elimination of ethane from {$PdMe_3I$(phen)} appears to occur at a slower rate than from the analogous bipy complex, although in the absence of kinetic data a quantitative comparison cannot be made.

Addition of MeI to a saturated acetone solution of {$PdMe_2$(phen)} at 0°C immediately produced a clear colourless solution from which a white crystalline solid could be isolated. This solid analysed correctly for {$PdMe_3I$(phen)}, and based on an N.M.R. spectrum in chloroform-D, figure 5.3.1-10, the structure portrayed in figure 5.3.1-11 is proposed, again featuring *trans* addition of the organohalide.

Figure 5.3.1-10. ^{1}H NMR of {$PdMe_3I(phen)$} in Chloroform-D.

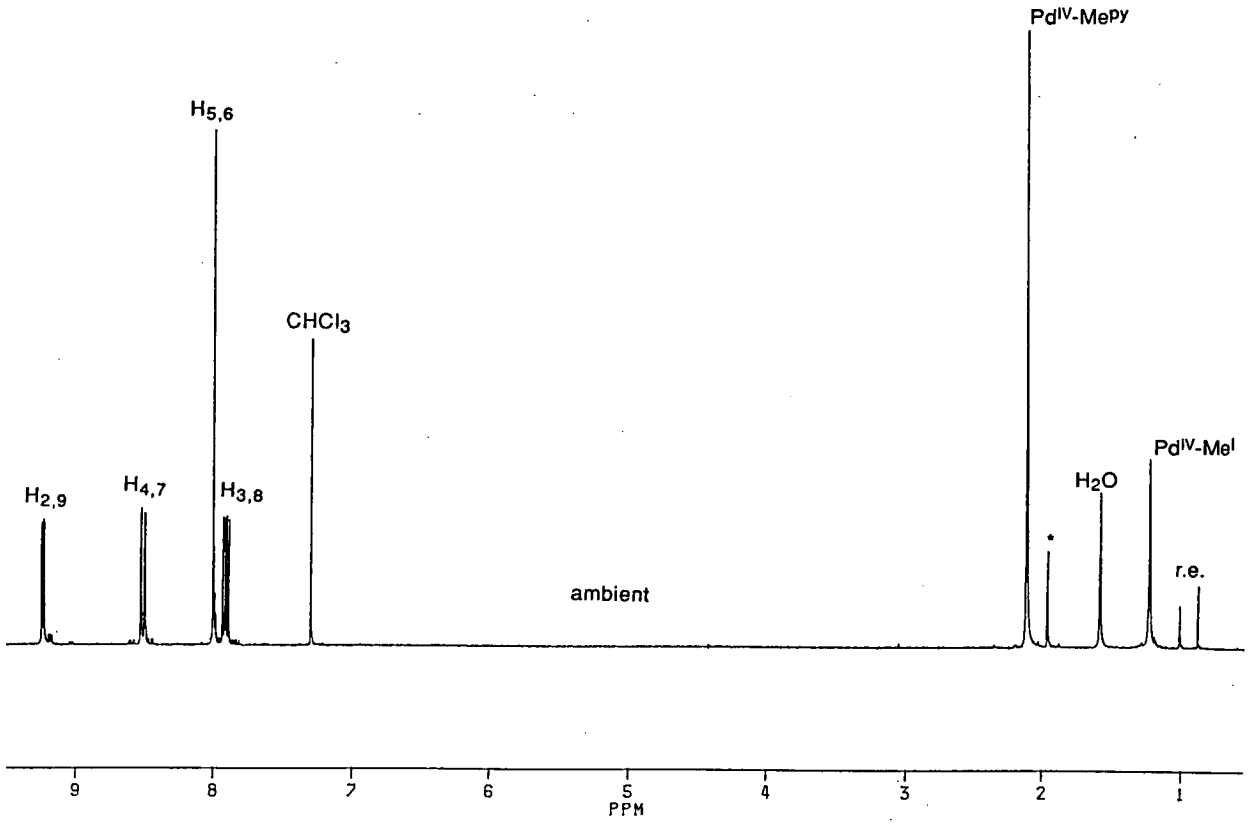
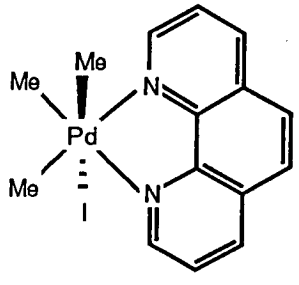


Figure 5.3.1-11.



5.3.2 Spectroscopically Detected Pd(IV) Complexes

Following the successful preparation, isolation and characterisation of the first alkylpalladium(IV) complexes {$PdMe_2RX(bipy)$} (RX=MeI, $PhCH_2Br$) and {$PdMe_3I(phen)$}, it was apparent that other palladium(IV) complexes containing bidentate ligands may be accessible, and perhaps isolable. Indeed, during this study numerous palladium(IV) complexes were generated and detected *in situ* but, for a

variety of reasons, could not be isolated. The preparative method used for the generation of the palladium(IV) containing solutions has been described (*vide supra*), and gives both neutral and cationic complexes depending upon the ligand and reaction solvent used.

5.3.2-i Neutral Complexes

Preparation of the neutral complexes {$PdMe_3I(L_2)$} (L_2=N-donor bidentate ligand) was achieved in all cases by an *in situ* reaction in acetone-D6, and for convenience the complexes are grouped according to the bridgehead-carbon functionality.

(a) Planar and sp^2- Carbon Bridged Ligands

Oxidative addition of MeI to an acetone solution of {$PdMe_2(L_2)$} (L=pymim, $mim_2C{=}CH_2$, pymimC=O) at -10°C immediately produced spectra which could be readily assigned as {$PdMe_3I(L_2)$}. Warming slowly to ambient temperature produced the corresponding reductive elimination product {$PdMeI(L_2)$} and ethane which could be removed by purging the solution with N_2. The complexes displayed stability lower than that for {$PdMe_3I$(bipy)} and {$PdMe_3I$(phen)}, indeed the complex {$PdMe_3I$(pymim)} required oxidative addition of MeI at -20°C to produce a spectrum displaying only small quantities of the reductive elimination products, whereas for {$PdMe_3I$(bipy)} this could be achieved at 0°C. An exception to this, however, is {$PdMe_3I$(pymimC=O)}, which is relatively stable at 0°C, although attempts to isolate this complex from a preparative scale reaction failed, probably as a result of its high solubility in acetone.

Spectra for the complexes are displayed in figures 5.3.2-1-4, and tabulated in table 5.3.2-1, with assignment of aromatic protons based on an earlier discussion (chapter 4). Assignment of Pd^{IV}-Me resonances for the complexes of unsymmetrical ligands follows directly from straightforward assignments for the complexes of symmetrical ligands. For the complex {$PdMe_3I(pymimC{=}CH_2)$}, assignment of the

Figure 5.3.2-1. ^{1}H NMR of {$PdMe_2(mim_2C{=}CH_2)$} + MeI in Acetone-D6.

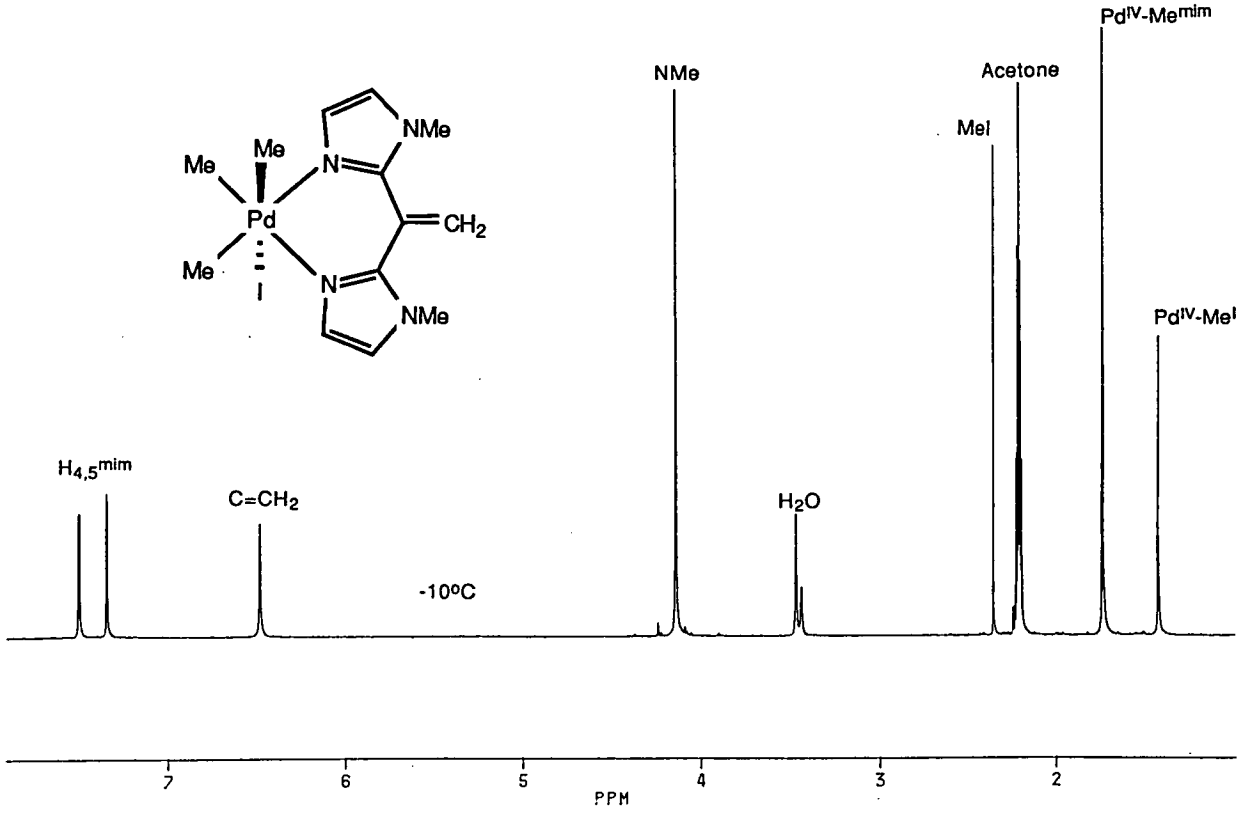


Figure 5.3.2-2. ^{1}H NMR of {$PdMe_2(pymim)$} + MeI in Acetone-D6.

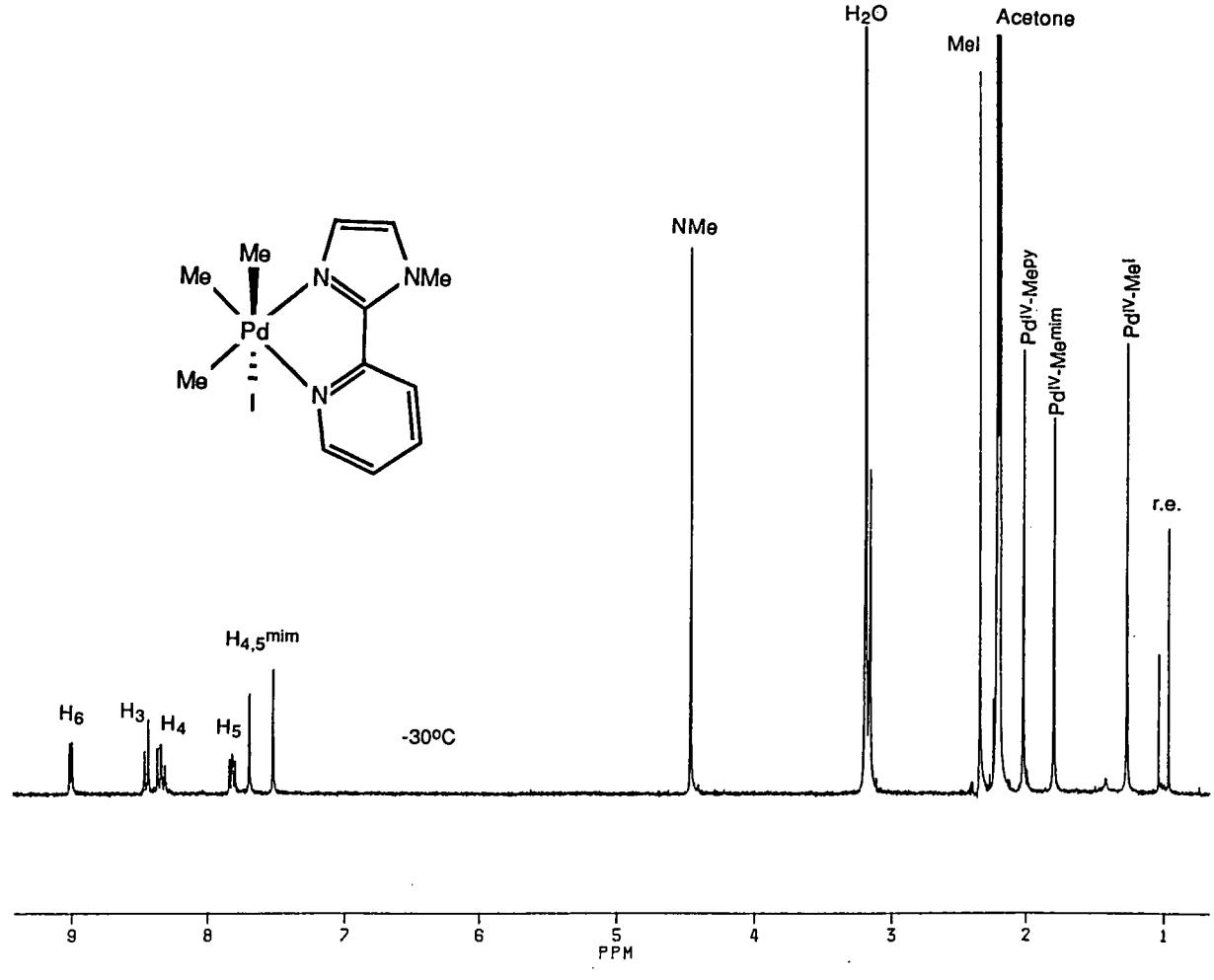


Figure 5.3.2-3. ^{1}H NMR of {$PdMe_2$(pymimC=O)} + MeI in Acetone-D6.

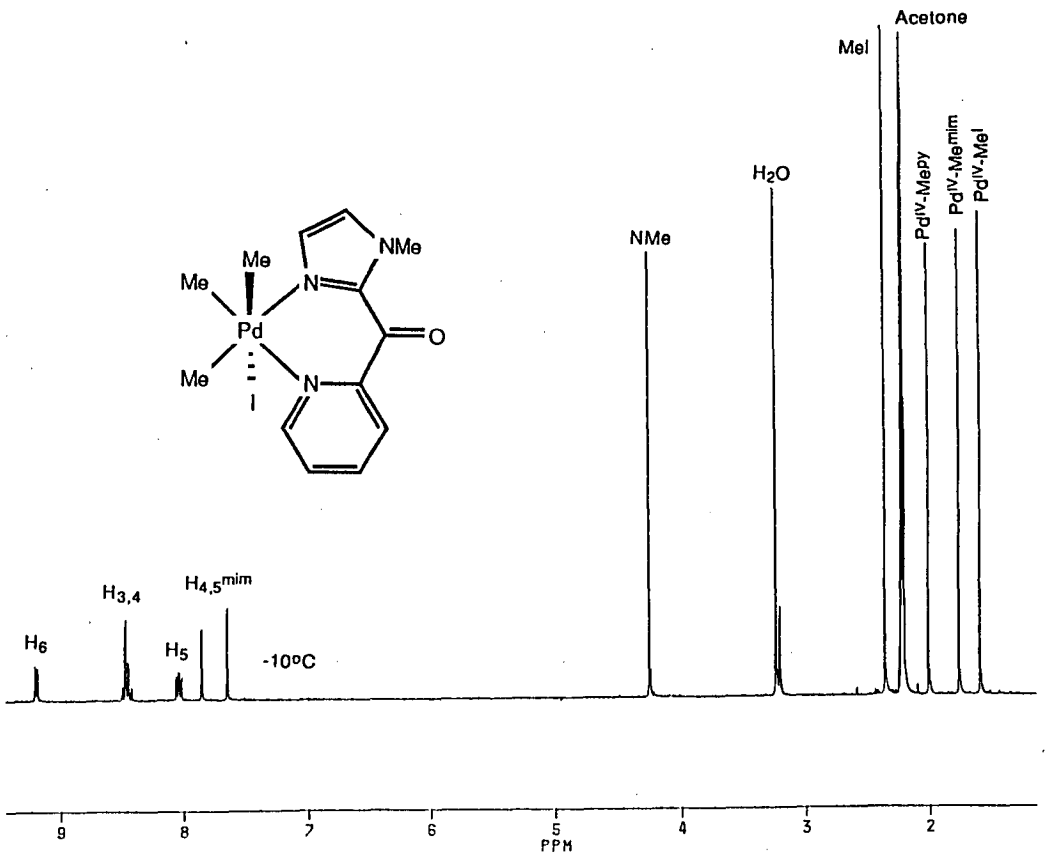


Figure 5.3.2-4. ^{1}H NMR of {$PdMe_2$(pymimC=CH_2)} + MeI in Acetone-D6.

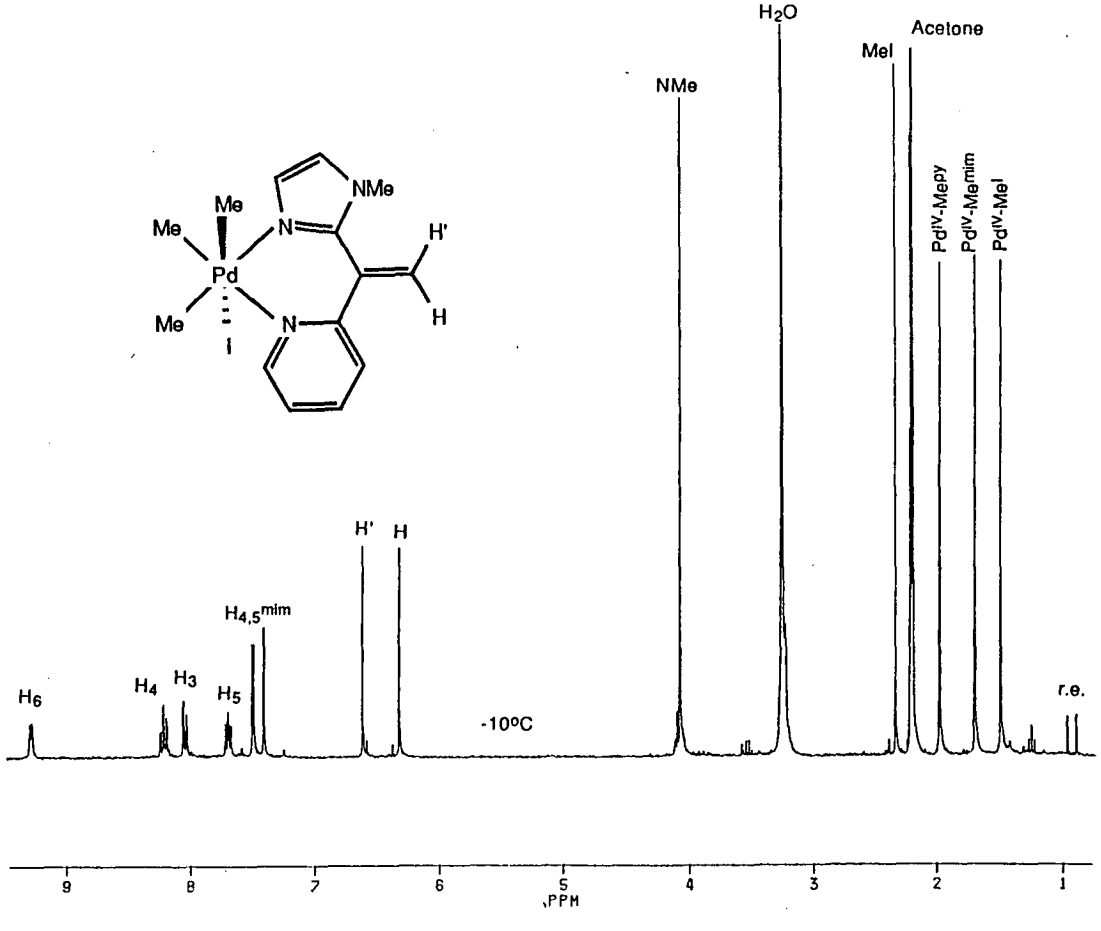


Table 5.3.2-1. ^1H NMR Chemical Shifts for $\{PdMe_3I(L_2)\}$ Complexes in Acetone-D6 at -10°C

L_2	Chemical Shifts δ (ppm) Aromatic Resonances	Pd-Me (*trans* group)	Other
$mim_2C{=}CH_2$	mim: 7.35($H_{4(5)}$), 7.20($H_{5(4)}$)	1.60 (mim) 1.29 (I)	4.00, NMe 6.34, $C{=}CH_2$
pymim[a]	py:8.86(H_6), 8.31(H_3), 8.20(H_4), 7.65(H_3) mim: 7.55($H_{4(5)}$), 7.38($H_{5(4)}$)	1.88 (py) 1.65 (mim) 1.13 (I)	4.32, NMe
pymimC=O	py:9.00(H_6), 8.32($H_{3,4}$), 7.92(H_5) Mim:7.76($H_{4(5)}$), 7.53($H_{5(4)}$)	1.82 (py) 1.57 (mim) 1.46 (I)	4.09, NMe
pymimC=CH	py:9.14(H_6), 8.07(H_4), 7.90(H_3), 7.56(H_5)	1.83 (py) 1.56 (mim) 1.35 (I)	3.93, NMe 6.48, C=CH' 6.18, C=CH

(a) spectrum recorded at -30°C

olefinic protons was also possible from a COSY spectrum with enhancement of long range effects, showing coupling of these protons to H_3 of pyridine and the N-Me group of imidazole.

The low solubility of $\{PdMe_2(mim_2C{=}O)\}$ in acetone, and the instability of $\{PdMe_2(py_2C{=}CH_2)\}$ in acetone, precluded studies of oxidative addition reactions of these complexes.

(b) Methane Bridged Ligands, R_2CH_2

Oxidative addition of MeI to $\{PdMe_2(pzmimCH_2)\}$, $\{PdMe_2(pz_2CH_2)\}$ and $\{PdMe_2(py_2CH_2)\}$ produced stable Pd(IV) complexes only at temperatures below -30°C, with reactions performed above this temperature giving spectra displaying the Pd(IV) complexes together with reductive elimination products. Spectra for the complexes are shown in figures 5.3.2-5-7 and listed in table 5.3.2-2, and are readily

Figure 5.3.2-5. ^{1}H NMR of {$PdMe_2(pzmimCH_2)$} + MeI in Acetone-D6.

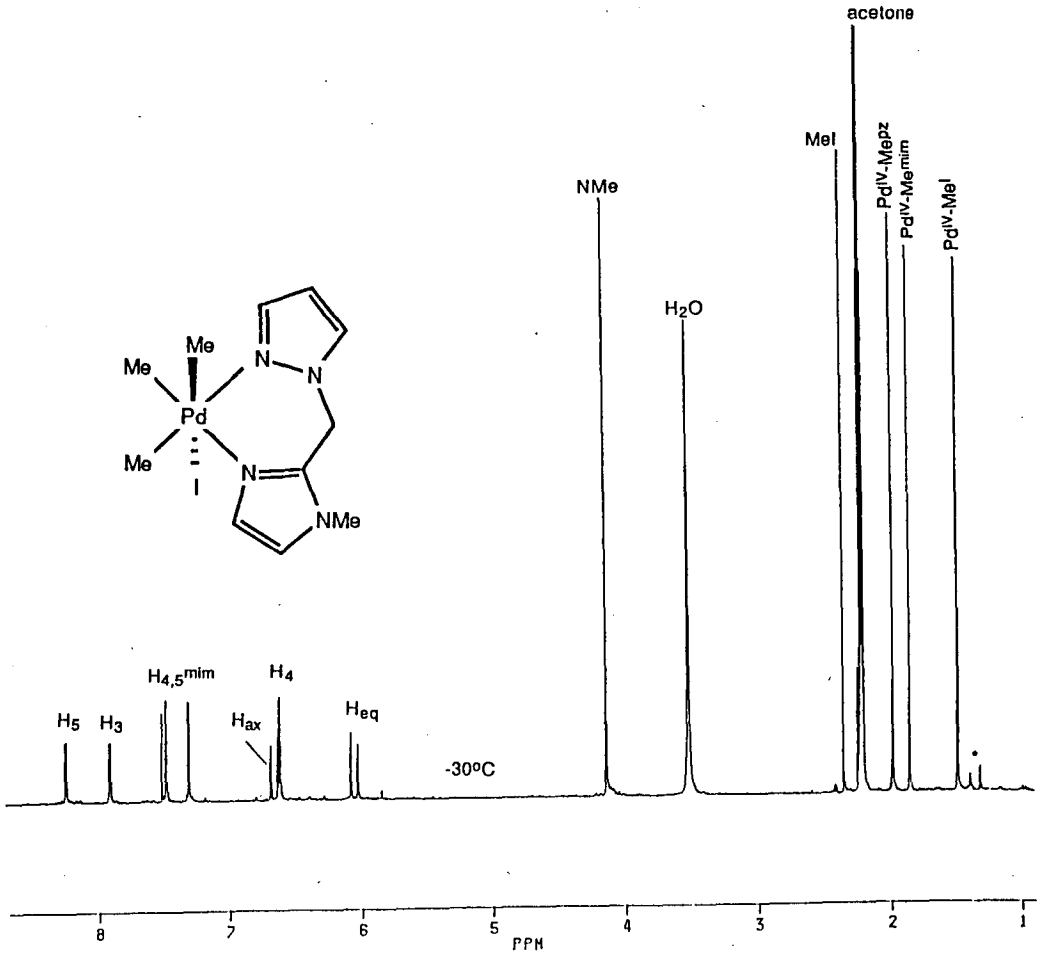


Figure 5.3.2-6. ^{1}H NMR of {$PdMe_2(pz_2CH_2)$} + MeI in Acetone-D6.

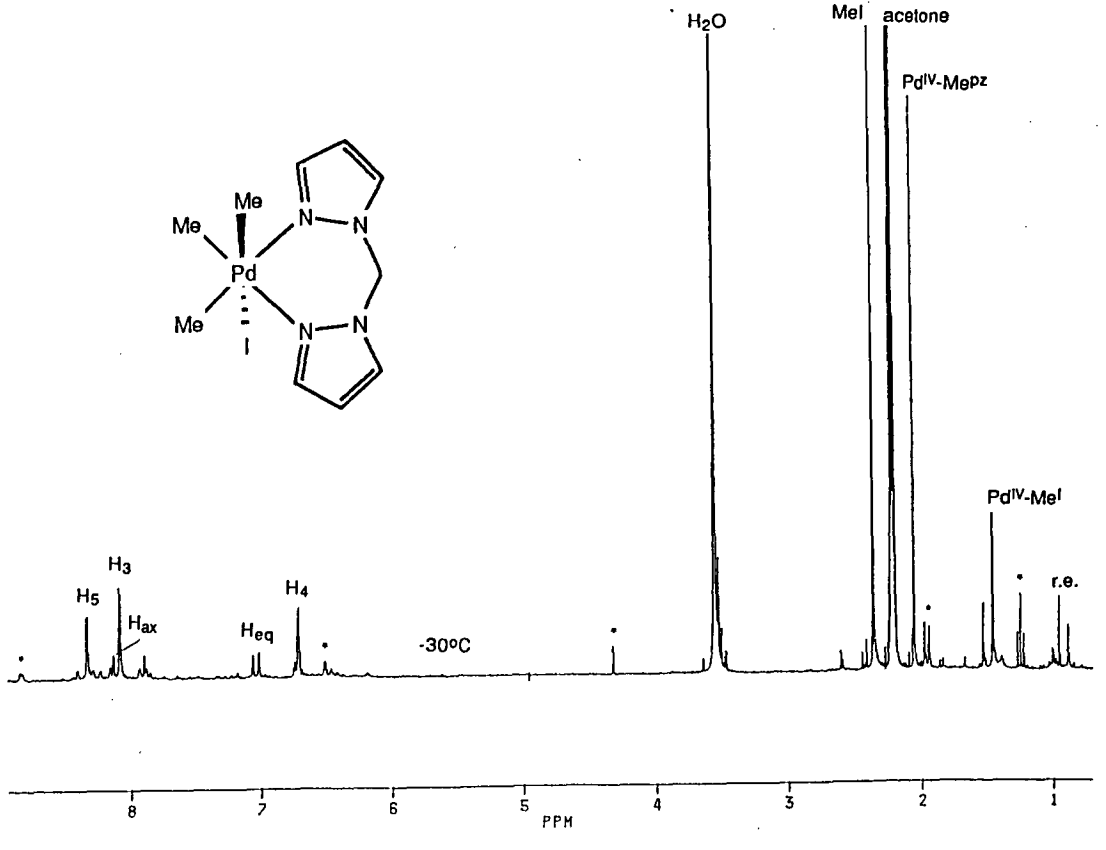


Figure 5.3.2-7. ^{1}H NMR of {$PdMe_2(pypzCH_2)$} + MeI in Acetone-D6.

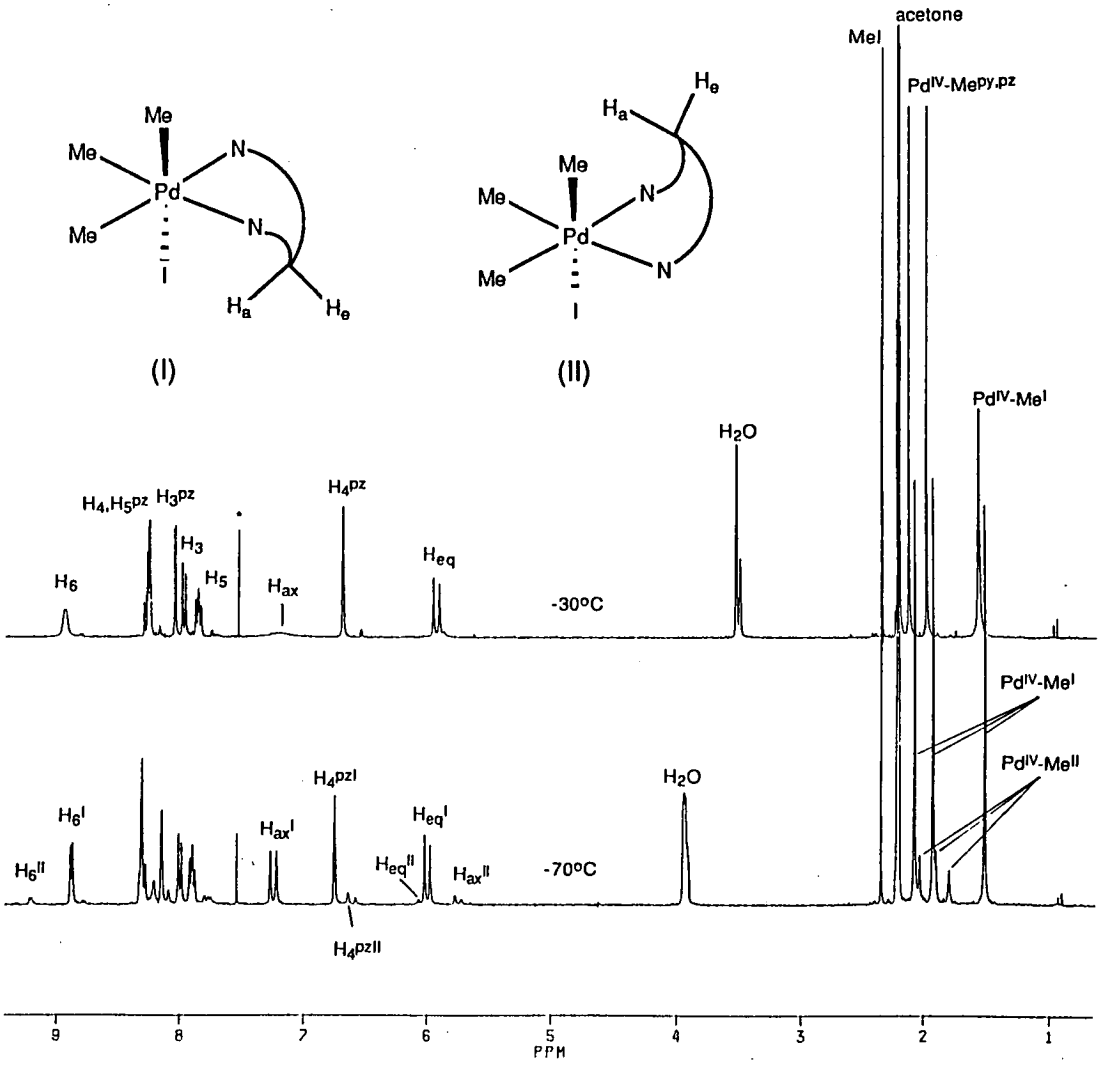


Table 5.3.2-2. ^{1}H NMR Chemical Shifts for {$PdMe_3I(L_2)$} Complexes in Acetone-D6 at -30°C

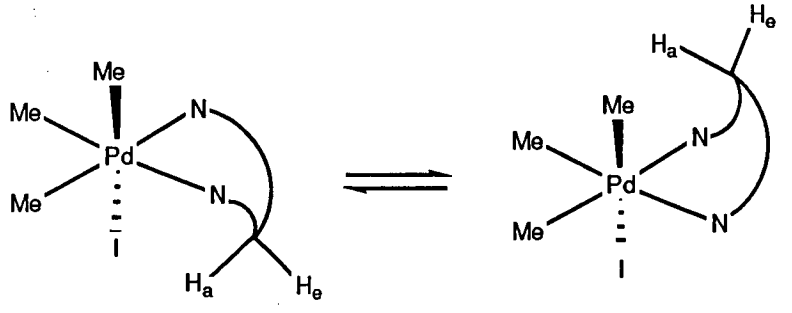
L_2	Chemical Shift δ (ppm) Aromatic Resonances	Pd-Me (*trans* group)	Other
pz_2CH_2	pz: 8.18(H_5), 7.93(H_2), 6.57(H_4)	1.91 (pz) 1.30 (I)	7.82, 6.89 CH_2 (^3J=15.4)
pzmimCH$_2$	pz: 8.11(H_5), 7.77(H_3), 6.48(H_4) mim: 7.34($H_{4(5)}$), 7.17($H_{5(4)}$)	1.84 (pz) 1.70 (mim) 1.33 (I)	7.02, 5.74 CH_2 (^3J=14.8) 4.00, NMe
pypzCH$_2$[a] I	py: 8.79(H_6), 8.12(H_4), 7.81(H_3), 7.69(H_5) pz: 8.08(H_5), 7.85(H_3), 6.51(H_4)	2.01 (py) 1.86 (pz) 1.43 (I)	7.02, 5.74 CH_2 (^3J=14.8)
II	py: 9.05(H_6), $H_{3,4\&5}$ obs. pz: 6.94(H_4), $H_{3,5}$ obs.	1.88 (py) 1.75 (pz) 1.65 (I)	~5.92, 5.60 CH_2 (^2J=14.0)

(a) Spectrum recorded at -70°C.

interpreted. The spectrum of $\{PdMe_3I(pz_2CH_2)\}$ contains several spurious resonances, indicated (*), arising from the instability of $\{PdMe_2(pz_2CH_2)\}$ and these resonances are present immediately prior to the addition of MeI.

The bridgehead protons for the complexes of $pzmimCH_2$ and pz_2CH_2 appear as doublets, and assuming that a boat conformation is adopted, the downfield doublet is assigned to the bridgehead proton in an axial orientation and adjacent to the iodo-group, since a deshielding effect of an adjacent iodo-group is expected. Consistent with this interpretation, the equatorial proton resonates at a similar position to that found in $\{PdMe_2(L_2)\}$. The spectrum of $\{PdMe_3I(pypzCH_2)\}$ at -30°C, on the other hand, displays one of the bridgehead protons as a sharp well resolved doublet and the other as a broad resonance. Cooling to -70°C resulted in resolution of this resonance to give a doublet, and the separation of a second set of resonances attributed to the conformational isomer formed upon boat to boat ring inversion, figure 5.3.2-8. The isomers occur in 7:1 ratio, and the major isomer has been assigned as I, based on the downfield shift of H_a^I (adjacent to iodide).

Figure 5.3.2-8.



The preference for conformer I can be rationalised on steric grounds. Although iodide and methyl have similar Van der Waals radii (Me=2.0Å,[76] I=1.98-2.04Å[77]), the Pd^{IV}-Me bond is shorter than the Pd^{IV}-I bond, for example in $\{PdMe_3I(bipy)\}$ Pd^{IV}-Me=2.040(6)Å and Pd^{IV}-I=2.834(1)Å, and thus the axial bridgehead proton experiences less steric interactions when adjacent to the Pd^{IV}-I group that the Pd^{IV}-Me

group, and indeed the orientation with an axial proton adjacent to iodide occurs in the related Pt(IV) complex {$PdMe_3I((3,5\text{-}Me_2\text{-}pz)_2CH_2)$}.[73]

Discussion of the palladium(IV) complexes formed from {$PdMe_2(py_2CH_2)$} and {$PdMe_2(pymimCH_2)$} may be found in section 5.3.2-ii, and the complex {$PdMe_2(mim_2CH_2)$} was too insoluble for formation of a palladium(IV) derivative.

(c) Ethane Bridged Ligands, R_2CHMe

Trans oxidative addition of methyliodide to a complex containing an ethane bridged ligand can theoretically yield two isomers, I and II in figure 5.3.2-9, which are not interconvertible by boat to boat ring inversion. The formation of two isomers is possible by S_N2 attack on MeI from either side of the palladium square plane, figure 5.3.2-10. Further, boat to boat ring inversion may potentially occur, to afford conformational isomers, but conformers Ib and IIb are considered unlikely as they would require the axial ligand methyl group to be adjacent to either a Pd^{IV}-Me or Pd^{IV}-I group, resulting in close steric interactions.

Figure 5.3.2-9.

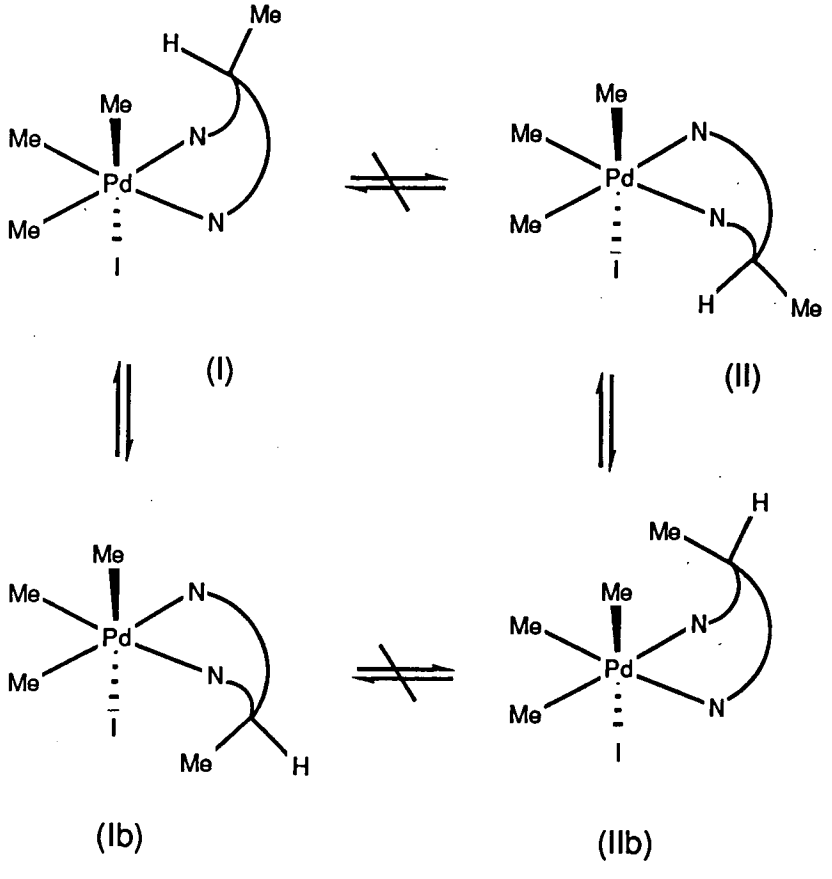
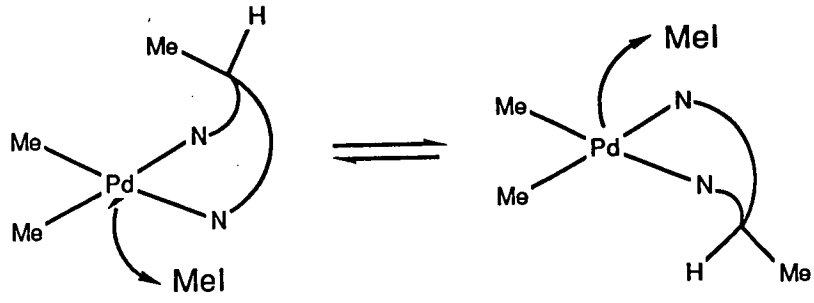


Figure 5.3.2-10.



Addition of MeI to {$PdMe_2(py_2CHMe)$} at -30°C produced, after *ca.* 20 minutes, a relatively complex spectrum exhibiting two Pd(IV) complexes in 1:1 ratio, figure 5.3.2-11. The spectrum did not change on cooling to -60°C, and gave only reductive elimination products (as additional species) on gradual warming to ambient temperature. The spectra are consistent with presence of isomers I and II, with one of the CH resonances *ca.* 2 ppm downfield from the other, and thus assigned as II, and a downfield shift for H_6 of isomer I (assigned from integration) presumably resulting from close proximity to the iodo-group with this boat conformation.

In contrast to the behaviour observed for {$PdMe_3I(py_2CHMe)$}, addition of MeI to {$PdMe_2(pz_2CHMe)$} at -30°C gave a spectrum (figure 5.3.2-12) displaying formation of isomer II only, *i.e.* with the CH group adjacent to the iodo-group, figure 5.3.2-13. This assignment is based on the large downfield shift (*ca.* 1.3 ppm) for the bridgehead proton in {$PdMe_3I(pz_2CHMe)$} compared with {$PdMe_2(pz_2CHMe)$}.

The conformational studies of {$PdMe_3I(py_2CHMe)$} and {$PdMe_3I(pz_2CHMe)$} raise interesting mechanistic questions. For example, is there a preferred face for oxidative addition and is this related to the conformational studies of the analogous $PdMe_2$(II) complexes, and does isomerisation to the ratio found occur during or after oxidative addition, and further, does isomerisation occur *via* a five coordinate intermediate? (These questions are addressed in section 5.7).

Figure 5.3.2-11. ^{1}H NMR of {$PdMe_2(py_2CHMe)$} + MeI in Acetone-D6.

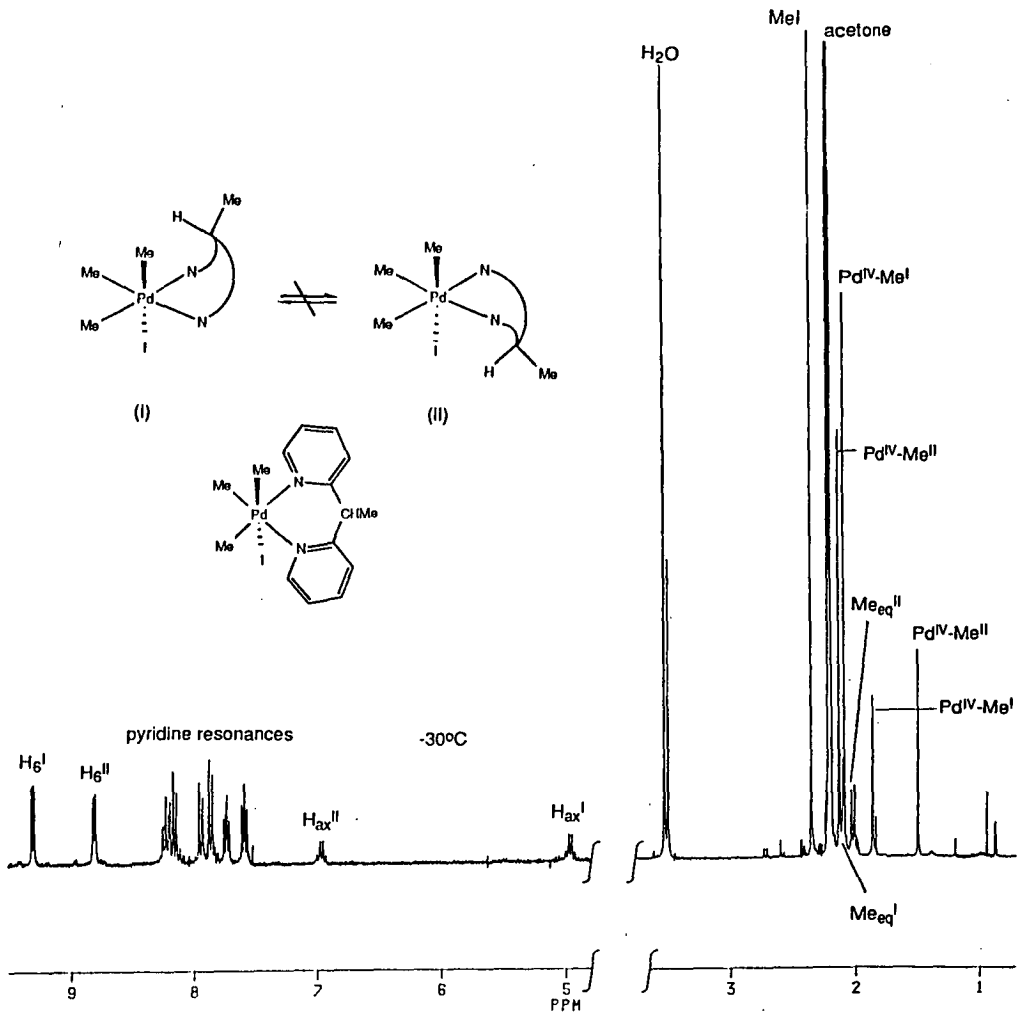
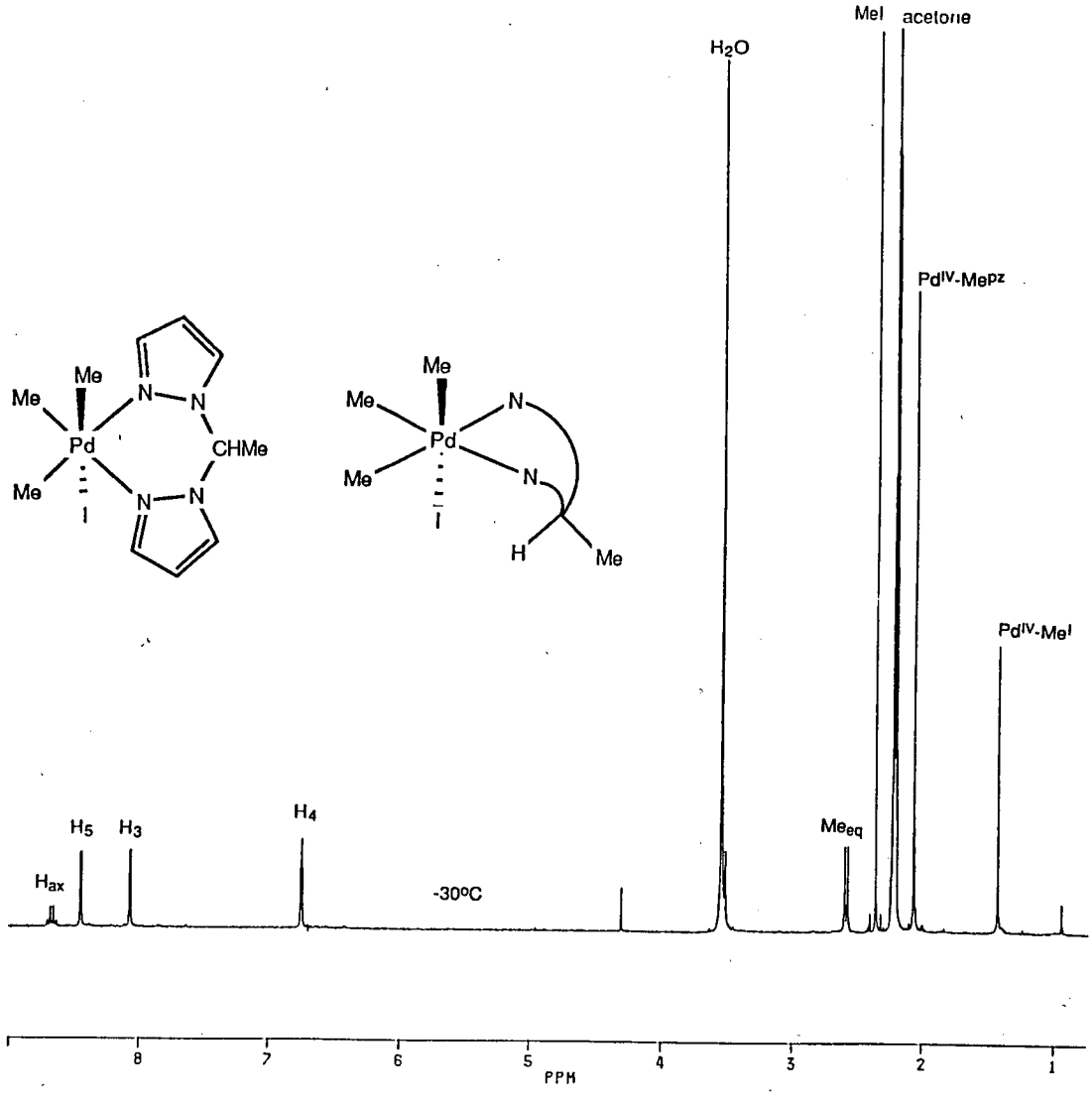


Table 5.3.2-3. ^{1}H NMR Chemical Shifts for {$PdMe_3I(R_2CHMe)$} Complexes in Acetone-D6 at -30°C.

L_2	Chemical Shifts δ (ppm) Aromatic Resonances	Pd-Me (*trans* group)	Other
py_2CHMe	*Isomer I* py: 9.16(H_6), 8.02(H_4), 7.72(H_2), 7.44(H_5)	1.94 (py) 1.73 (I) (^3J=7.48)	4.82, CH 1.97, CMe
	Isomer II py: 8.66(H_6), 8.08(H_4), 7.79(H_3), 7.59(H_5)	1.99 (py) 1.34 (I)	6.82, CH 1.88, CMe (^3J=7.11)
pz_2CHMe	pz: 8.33 (H_5), 7.96 (H_3), 6.63(H_4)	1.90 (pz) 1.28 (I)	8.48, CH 2.45, CMe (^3J=6.81)

Figure 5.3.2-12. ^{1}H NMR of {$PdMe_2(pz_2CHMe)$} + MeI in Acetone-D6.



(d) Propane Bridged Ligands, R_2CMe_2

Oxidative addition of MeI to {$PdMe_2(pz_2CMe_2)$} occurred slowly at -50°C to produce a spectrum which, in the aromatic region, displayed both the palladium(II) reactant and palladium(II) product, together with an additional pyrazole resonance. Assignment of CMe (ligand) and Pd^{IV}-Me resonances, however, was not possible owing to the broadness and complexity of the aliphatic region. A similar reaction between MeI and {$PdMe_2(py_2CMe_2)$} also proceeded slowly, as gauged by the disappearance of the Pd^{II}-Me resonance, but gave only very minor resonances attributable to an additional pyridine environment and, perhaps, Pd^{IV}-Me at 1.70 ppm, suggesting rapid reductive elimination. Indeed, Pd(IV) complexes of pz_2CMe_2 and

py_2CMe_2 are expected to be less stable than all other complexes studied, due to close Pd^{IV}-Me or Pd^{IV}-I···CMe interactions.

5.3.2-ii Cationic Complexes

The formation of cationic complexes was observed for planar and sp^2-carbon bridged ligands in acetonitrile-D3, and for methane and ethane bridged ligands in acetone-D6.

(a) Planar and sp^2-Carbon Bridged Ligand Complexes in MeCN

Following the preparation and detection of the cationic complexes $[PdMe_3(CD_3CN)(L_2)]I$ (L_2=bipy, phen) similar *in situ* reactions were performed on the complexes $\{PdMe_2(L_2)\}$ containing the planar sp^2-carbon bridged ligands $mim_2C{=}CH_2$, pymimC=CH_2 and pymimC=O. Addition of MeI to an acetonitrile-D3 solution of $\{PdMe_2(L_2)\}$ at -35°C immediately gave spectra displaying the presence of neutral and cationic complexes, figures 5.3.2-14-16. These spectra displayed similar variable temperature behaviour to that observed for $\{PdMe_3I(bipy)\}$, *e.g.* on warming to *ca.* -25°C the Pd^{IV}-Me resonances attributed to the cation $[PdMe_3(CD_3CN)(mim_2C{=}CH_2)]I$ are coalesced, indicating scrambling of the Pd^{IV}-Me groups, while further warming to *ca.*-10°C resulted in coalescence of the Pd^{IV}-Me resonances and N-methylimidazole resonances, indicating exchange between neutral and cationic complexes, figure 5.3.2-16.

Chemical shift positions for the complexes $\{PdMe_3I(L_2)\}$ and $[PdMe_3(CD_3CN)(L_2)]I$ are listed in table 5.3.2-4.

Table 5.3.2-4. Chemical Shift Positions for the Complexes $[PdMe_3(CD_3CN)(L_2)]I$ and $\{PdMe_3I(L_2)\}$ in Aectonitrile-D3 at -35°C

L_2	Neutral Cation	Chemical Shift δ (ppm) Aromatic (*trans* group)	Pd-Me	Other
bipy	N	py: 8.89(H_6), 8.46(H_3), 8.18(H_4), 7.70(H_5)	1.79 (py) 1.20 (I)	
	C	py: 8.81(H_6), 8.54(H_3), 8.29(H_4), 7.80(H_5)	1.59 (py) 1.06 (CD_3CN)	
		N:C *ca* 3:1		
phen	N	py: 9.24($H_{2,9}$), 8.74($H_{4,7}$), 8.19($H_{5,6}$), 8.04($H_{3,8}$)	1.93 (py) 1.26 (I)	
	C	py: 9.17($H_{2,9}$), 8.82($H_{4,7}$), 8.24($H_{5,6}$), 8.11($H_{3,8}$)	1.73 (py) 1.13 (CD_3CN)	
		N:C *ca* 5:2		
pymim C=0	N	py: 9.0(H_6), 8.35(H_3), 8.26(H_4), 7.85(H_5) mim: 7.55($H_{4(5)}$), 7.51($H_{5(4)}$)	1.89 (py) 1.66) (mim, 1.63) I)	
	C	py: 8.87(H_6), 8.40(H_4), 8.35(H_3), 7.95(H_5) mim:7.65($H_{4(5)}$), 7.51($H_{5(4)}$)	1.44) (py, 1.43) mim, ?) CD_3CN)	
		N:C *ca* 5:1		
pymim C=CH_2	N	py: 9.12(H_6), 8.13(H_4), 7.92(H_3), 7.64(H_5)	1.83 (py) 1.56 (mim) 1.43 (I)	6.42,) 6.11) C=CH_2 3.83, NMe
	C	py: 8.66(H_6), 8.03(H_4), 7.82(H_3), 7.52(H_5)	1.59) (py, 1.31) mim, ?) CD_3CN)	6.37) 6.04) C=CH_2 3.82, NMe
	N,C	mim: 7.34($H_{4(5)}$), 7.30($H_{4(5)}$), 7.26($H_{4(5)}$) 7.22($H_{4(5)}$)		
		N:C *ca* 4:3		
$mim_2C=CH_2$	N	mim: 7.34($H_{4(5)}$), 7.18($H_{5(4)}$)	1.60 (mim) 1.37 (I)	6.19,C=CH_2 3.84,NMe
	C	mim: 7.24($H_{4,5}$)	1.36 (mim) 1.29 (CD_3CN)	6.28,C=CH_2 3.86, NMe

Figure 5.3.2-14. ^{1}H NMR of {$PdMe_2$(pymimC=O)} + MeI in Acetonitrile-D3.

Fic trile-D3.

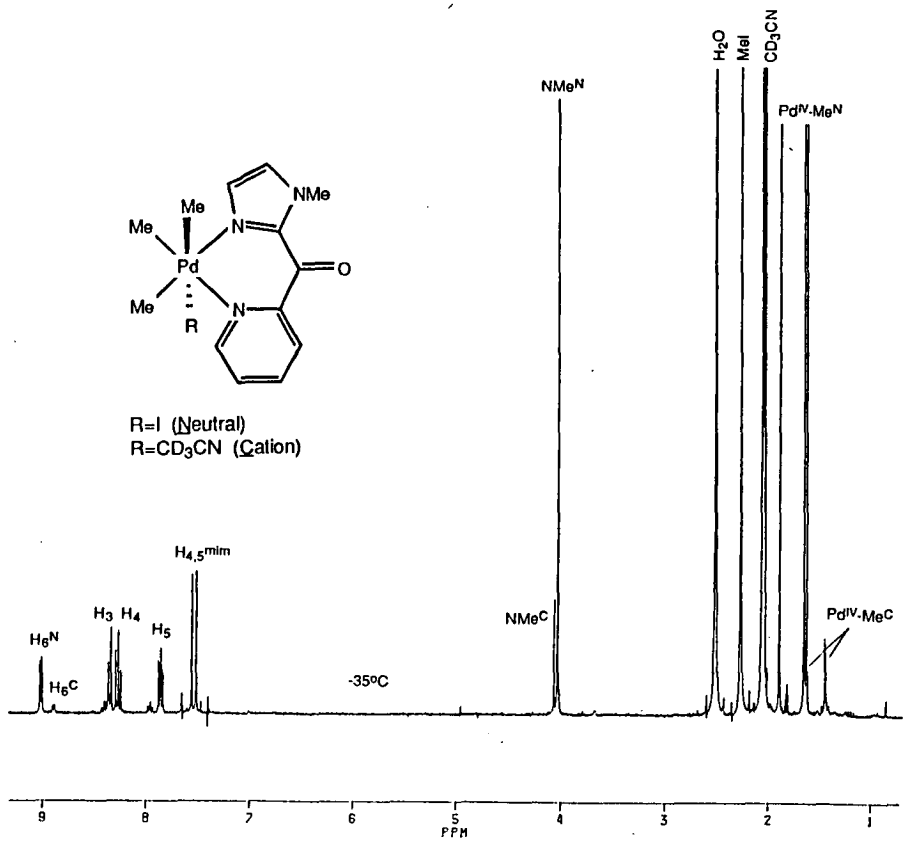


Figure 5.3.2-15. ^{1}H NMR of {$PdMe_2$(pymimC=CH_2)} + MeI in Acetonitrile-D3.

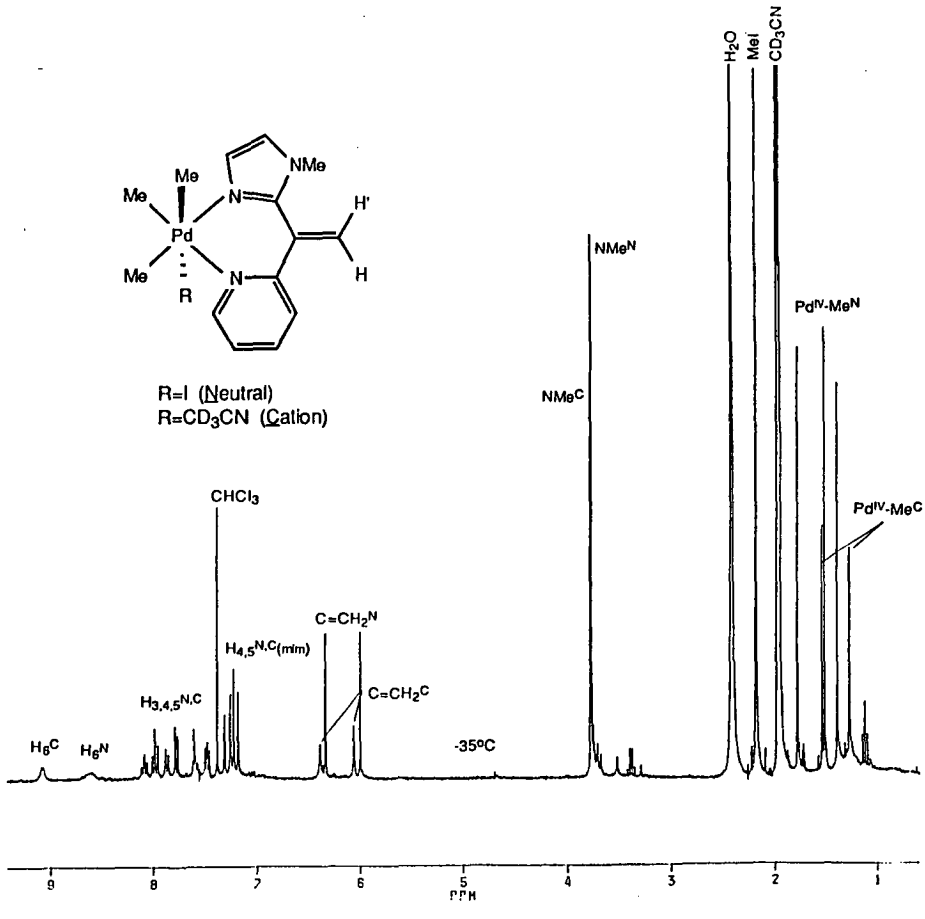
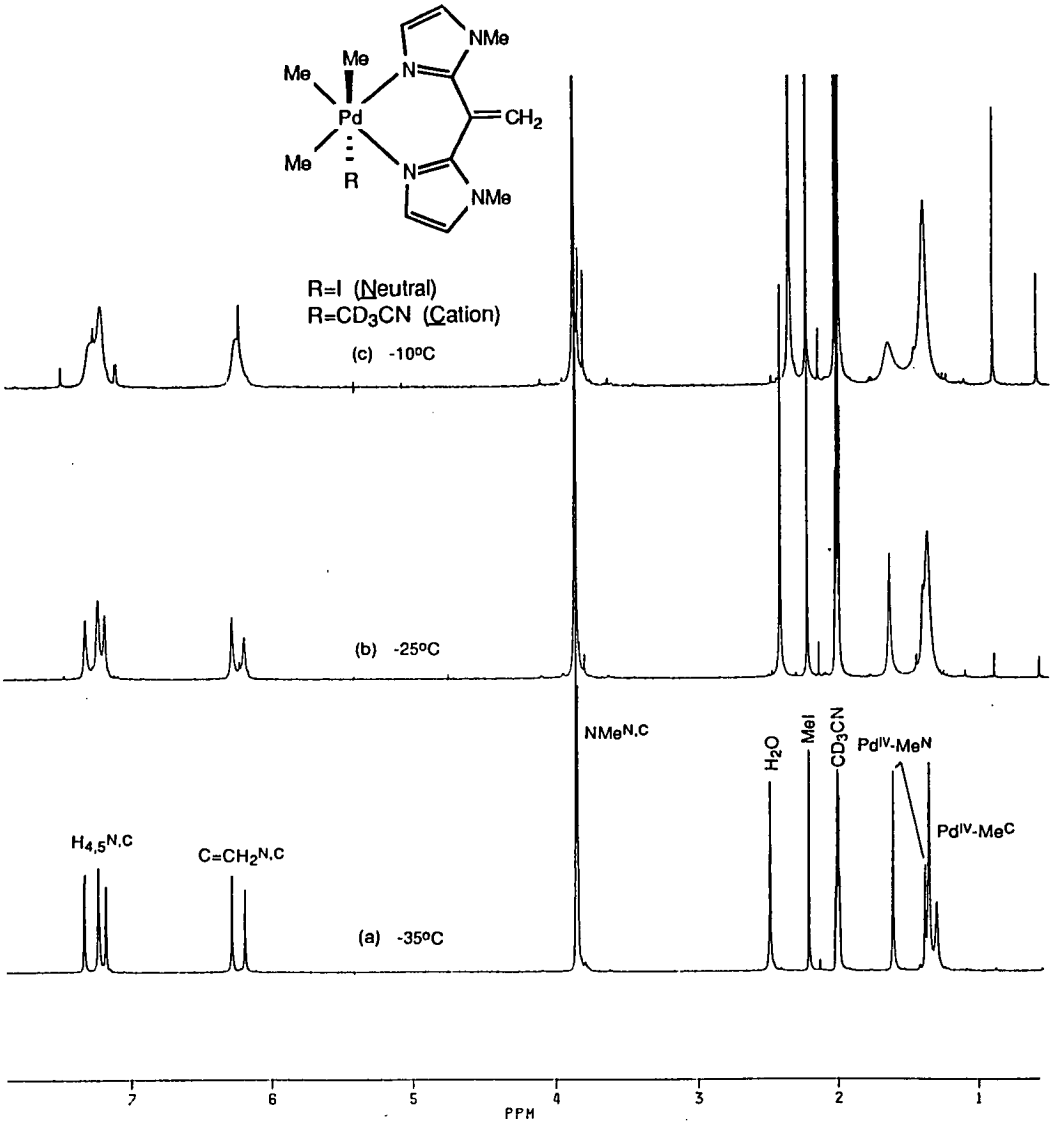


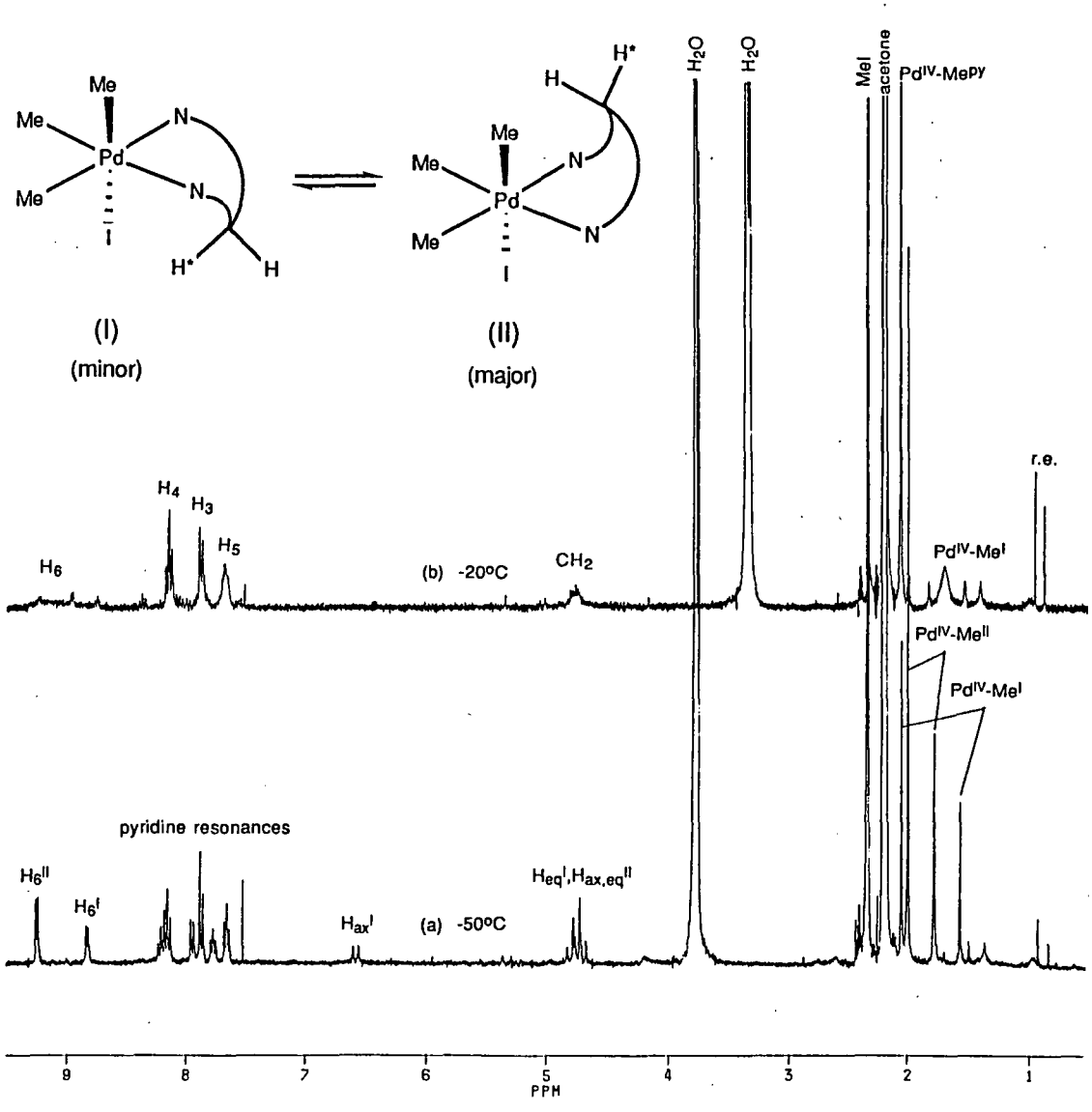
Figure 5.3.2-16. ^1H NMR of $\{PdMe_2(mim_2C{=}CH_2)\}$ + MeI in Acetonitrile-D3.



(b) Methane and Ethane Bridged Ligand Complexes in Acetone

Oxidative addition of MeI to $\{PdMe_2(py_2CH_2)\}$ at -20°C occurred immediately to give a spectrum exhibiting broad resonances for the H_5, H_6, CH_2 (bridgehead) and Pd^{IV}-Me protons, but with the remaining resonances sharp and well resolved, including a Pd^{IV}-Me resonance at 1.92 ppm, figure 5.3.2-17. Cooling resulted in further broadening and gradual separation of resonances, until at -50°C resonances for two distinct complexes in *ca.* 3:2 ratio could be discerned. This process was reversible, and may be interpreted in terms of boat to boat ring inversion between conformational isomers.

Figure 5.3.2-17. ^1H NMR of $\{PdMe_2(py_2CH_2)\}$ + MeI in Acetone-D6.



The minor conformer present has been assigned as (I), based on the downfield shift of H_a^I (adjacent to iodide) compared with H_a^{II} (adjacent to methyl). Consistent with this assignment H_6^{II}, which is beneath the 'Me_2PdN_2' plane and **adjacent** to the iodo-group, is deshielded compared with H_6^I, which is above this plane and **away** from the iodo-group. It is interesting that a preference for conformer II is observed for $\{PdMe_3I(py_2CH_2)\}$, while for $\{PdMe_3I(pz_2CH_2)\}$ and $\{PdMe_3I(pzmimCH_2)\}$

conformer I is preferred, and this behaviour may be related to increased puckering of the chelate ring of py_2CH_2.

Slow warming to +10°C produced {$PdMeI(py_2CH_2)$} and ethane, together with another palladium(IV) complex which exhibited two Pd^{IV}-Me resonances in 2:1 ratio, and a sharp singlet for the bridgehead protons, figure 5.3.2-18. Upon cooling, the original palladium(IV) complex was not re-formed, and the resonance for the bridgehead protons broadened but did not resolve to a pair of doublets. Based on this behaviour the formation of a cation is proposed, figure 5.3.2-19, and consistent with this interpretation the bridgehead protons are not deshielded, as found for $H_a{}^I$. The nature of the solvent molecule in (III) is not known, and could conceivably be MeI,[56b,78] acetone-D6, or H_2O (present in acetone).

Figure 5.3.2-18. ^1H NMR of {$PdMe_2(py_2CH_2)$} + MeI in Acetone-D6.

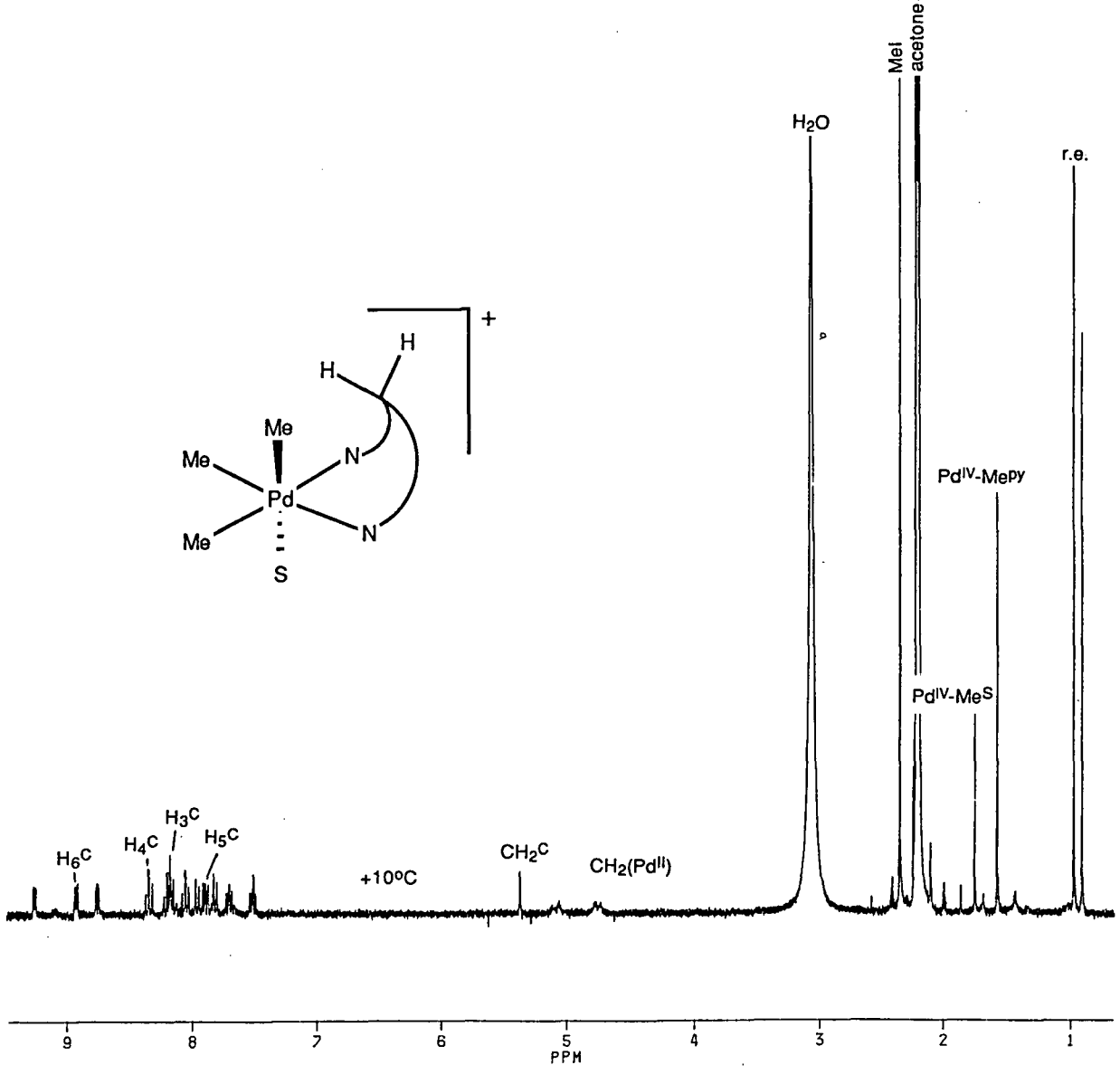
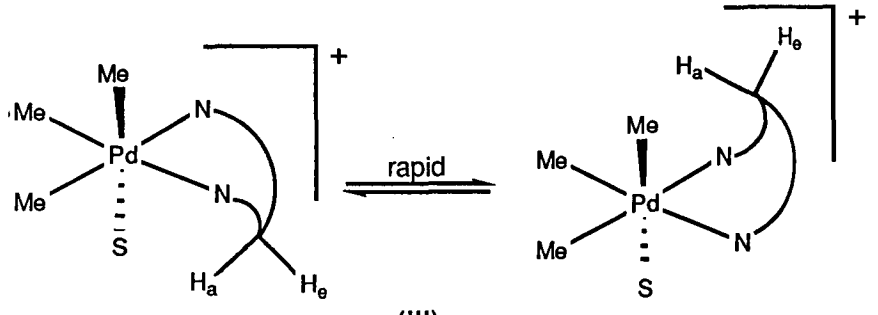


Figure 5.3.2-19.



(III)

For the neutral complex {$PdMe_3I(pymimCH_2)$}, formed from an *in situ* oxidative addition reaction at -30°C, boat to boat interconversion was not observed, but warming to *ca.* -10°C slowly produced a second complex, together with reductive elimination products, with three new Pd^{IV}-Me resonances and a sharp singlet for the bridgehead protons, figure 5.3.2-20. Cooling to -60°C resulted in broadening of the bridgehead protons, but did not produce the original palladium(IV) complex, and formation of the cationic complex [$PdMe_3(S)(pymimCH_2)$]I is proposed.

The formation of a palladium(IV) complex was also observed upon an *in situ* reaction between MeI and {$PdMe_2(pymimCHMe)$} at -40°C, figure 5.3.2-21. In this case, however, a shift to lower field was not observed for the bridgehead proton or methyl group, indicating CH and CMe are not adjacent to the iodo-group. Further, studies on the related $PdMe_2$(II) and PdMeI(II) analogues (section 4.2.(1,2)) revealed that the bridgehead methyl groups **do not** assume an equatorial orientation, owing to steric interactions with the N-Me group of imidazole. Thus, a structure with these groups in an axial orientation is likely and either a neutral complex with the CMe group adjacent to the Pd^{IV}-Me group (I) or a cation with CMe adjacent to a solvent molecule (II) are possible, figure 5.3.2-21. The formation of [$PdMe_3(S)(pymimCHMe)$]I is favoured, since structure I would be expected to exhibit a close Pd^{IV}-Me....C-Me interaction.

Figure 5.3.2-20. ^{1}H NMR of {$PdMe_2(pymimCH_2)$} + MeI in Acetone-D6.

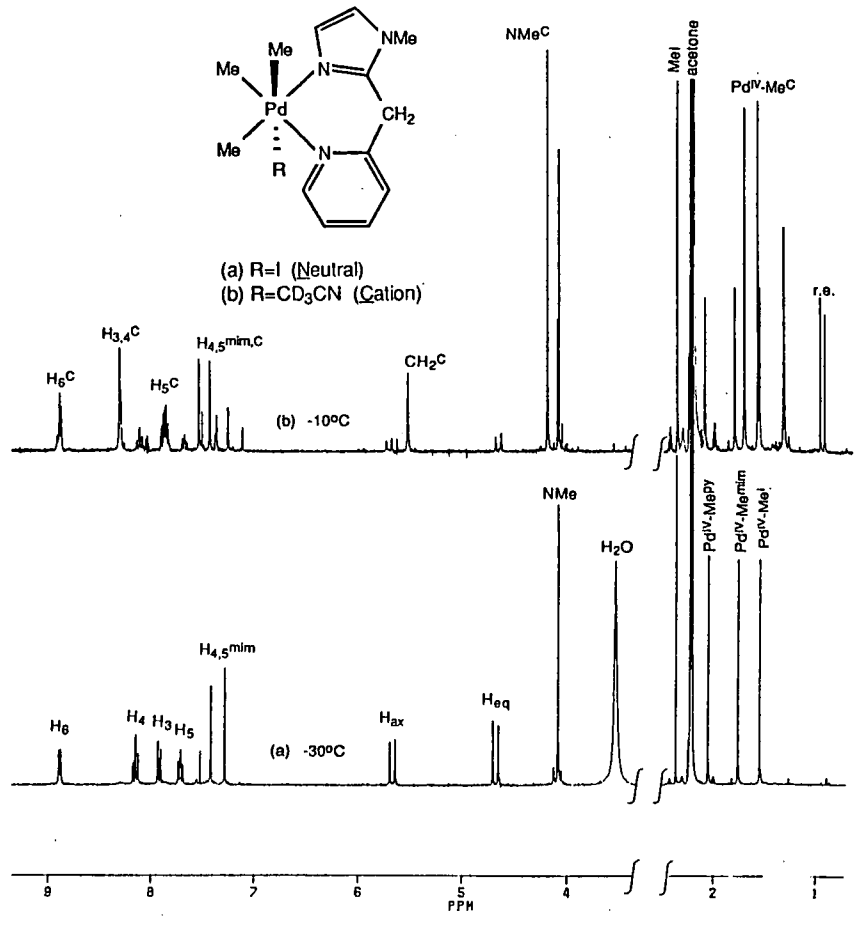
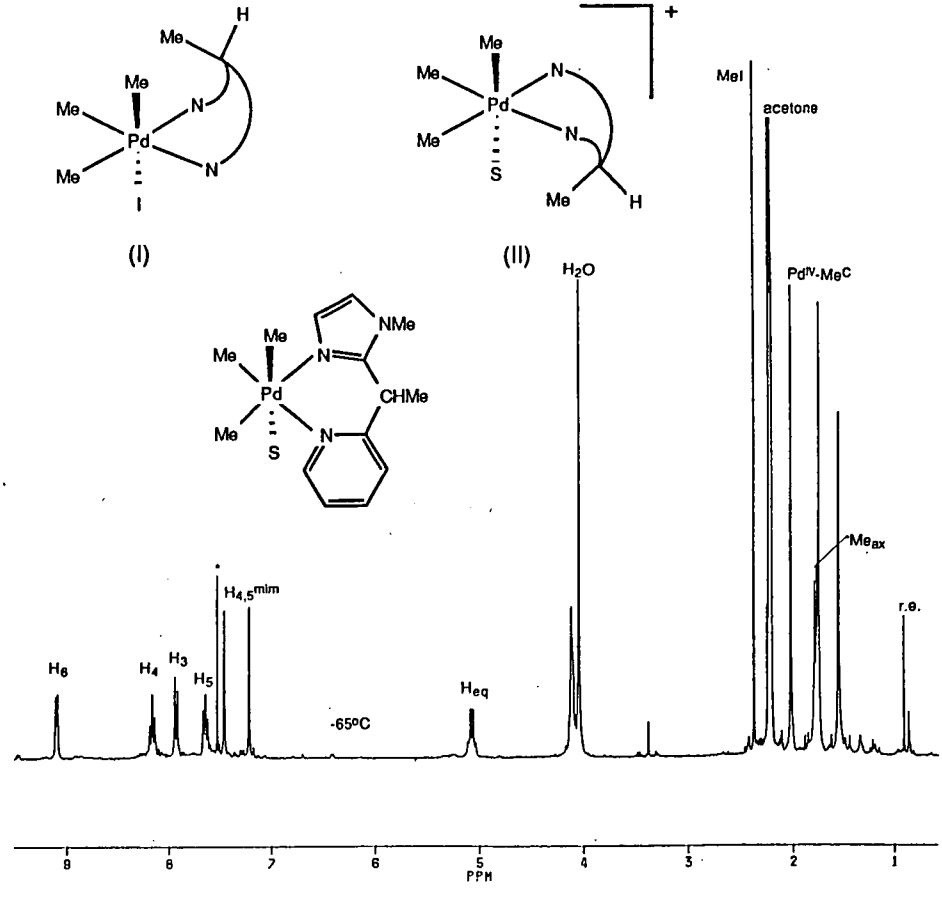
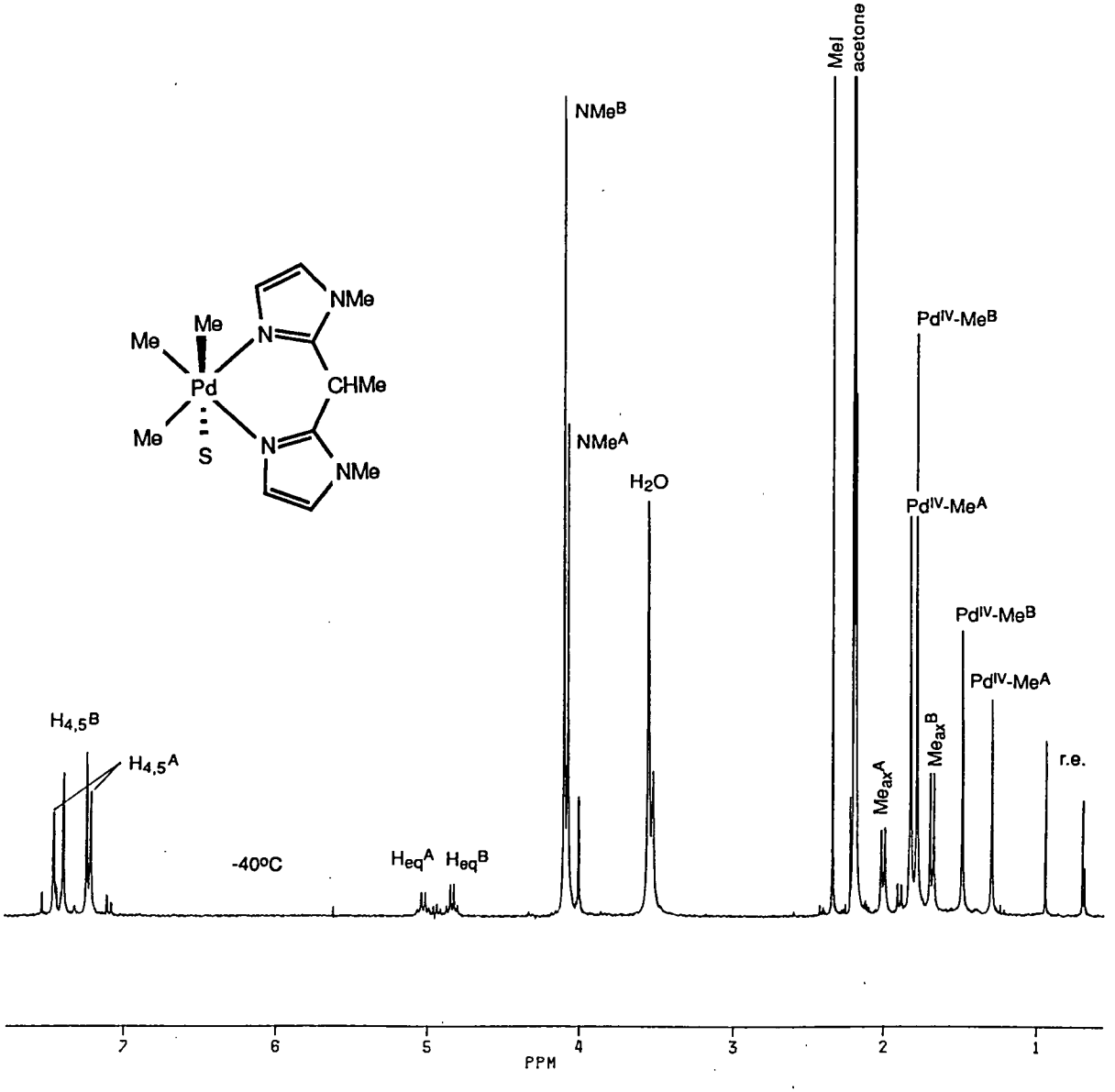


Figure 5.3.2-21. ^{1}H NMR of {$PdMe_2(pymimCHMe)$} + MeI in Acetone-D6.



For {$PdMe_2(mim_2CHMe)$}, oxidative addition of MeI resulted in the formation of two palladium(IV) complexes (A,B), whose relative proportions and chemical shifts did not change on cooling or warming, figure 5.3.2-22. This complex is also expected to exhibit the CMe group in an axial orientation, and the spectrum is consistent with structure I together with structure II, which do not interconvert, or the formation of two different cationic complexes. The latter is favoured, however, as the former would be expected to exhibit close Pd^{IV}-Me····C-Me interactions.

Figure 5.3.2-22. ^1H NMR of {$PdMe_2(mim_2CHMe)$} + MeI in Acetone-D6.



Chemical Shift positions for the complexes $[PdMe_3(S)(L_2)]I$ and {$PdMe_3I(L_2)$} are listed in table 5.3.2-5.

Table 5.3.2-5. Chemical Shift Positions for {$PdMe_3I(L_2)$} and $[PdMe_3(S)(L_2)]I$ Complexes in Acetone-D6

L_2	Neutral Cation	Chemical Shift δ (ppm) Aromatic *(trans group)*	Pd-Me	Other
py_2CH_2	N[a], I	py: 8.68(H_6), 8.07(H_4), 7.81(H_3), 7.63(H_5)	1.90 (py) 1.42 (I)	6.44, ~4.6 **CH_2** (^2J=13.9)
	II	py: 9.10(H_6), 8.02(H_4), 2.73(H_3), 7.52(H_5)	1.85 (py) 1.64 (I)	~4.60, **CH_2**
		conformer I:II *ca* 4:7		
	C[b]	py: 8.78(H_6), 8.20(H_4), 8.02(H_3), 7.75(H_5)	1.61 (S) 1.41 (py	5.23, **CH_2**
$pymimCH_2$	N[c]	py: 8.74(H_6), 7.99(H_4), 7.76(H_3), 7.55(H_5) mim: 7.26($H_{4(5)}$), 7.12($H_{5(4)}$)	1.91 (py) 1.64 (mim) 1.41 (I)	3.93, **NMe** 5.52, 4.52 **CH_2** (^2J=15.9)
	C[d]	py: 8.73(H_6), 8.26(H_3), 8.14(H_4), 7.72(H_5) mim: 7.42($H_{4(5)}$), 7.27 $H_{(5(4)}$)	1.60) (py, 1.48) mim 1.21) S)	4.07, **NMe** 5.45, **CH_2**
pymimCHMe	C[e]	py: 8.95(H_6), 8.03(H_4), 7.79(H_3), 7.05(H_5) mim: 7.32($H_{4(5)}$), 7.08($H_{5(4)}$)	1.87) (py, 1.58) mim, 1.38) S)	3.9, **NMe** 4.93, **CH** 1.61, **CMe**
mim_2CHMe	C[e], A	mim: 7.31($H_{4(5)}$), 7.07($H_{5(4)}$)	1.68 (mim) 1.14 (?)	3.93, **NMe** 4.88, **CH** 1.86, **CMe** (^3J = 7.27)
	B	mim: 7.25($H_{4(5)}$), 7.09($H_{5(4)}$)	1.64 (mim) 1.38 (?)	3.96, **NMe** 4.69, **CH** 1.54, **CMe**
		A : B *ca.* 5 : 6		(^3J=7.3)

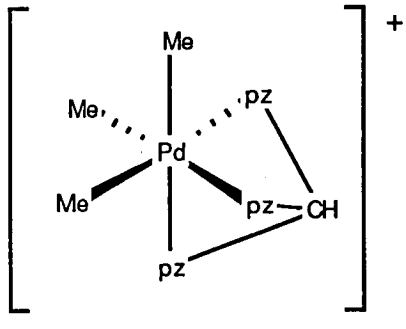
Temperature : (a) -50°C; (b) 10°C; (c) -30°C; (d) -10°C; (e) -40°C

5.4 ALKYLPALLADIUM(IV) COMPLEXES WITH TRIDENTATE LIGANDS

5.4.1 Preliminary Studies

An *in situ* oxidative addition reaction between {$PdMe_2(pz_3CH)$} and MeI at ambient temperature immediately gave a spectrum showing the presence of a palladium(IV) complex. The complex displayed **one** pyrazole ring environment and one Pd^{IV}-Me resonance at 1.58 ppm, and underwent slow reduction elimination of ethane to form {$PdMeI(pz_3CH)$}, with a spectrum obtained after 20 hours exhibiting *ca.* 10% of the palladium(IV) complex. The spectrum is clearly consistent with a cationic structure, with a *facial* arrangement for both the Pd^{IV}-Me and pyrazole groups, figure 5.4.1-1. Similar structures have been proposed for the analogous trimethylplatinum(IV) complexes $[PtMe_3(pz_3CH)]PF_6$,[73] and {$PtMe_3(pz_3BH)$}.[79]

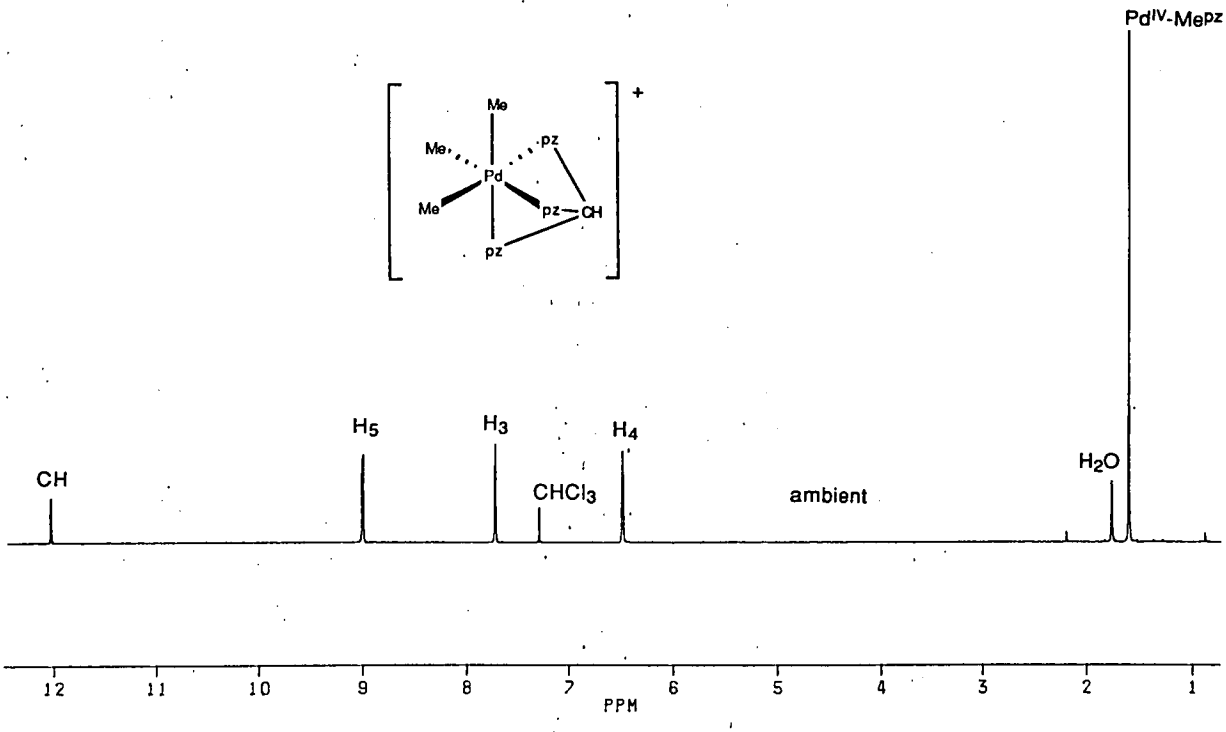
Figure 5.4.1-1



In view of the high stability exhibited by $[PdMe_3(pz_3CH)]I$ a preparative reaction was attempted, and upon addition of MeI to a concentrated acetone solution of {$PdMe_2(pz_3CH)$} at 0°C a white highly crystalline solid formed. This solid analysed correctly for $[PdMe_3(pz_3CH)]I$, and although not readily soluble in acetone-D6, a spectrum in chloroform-D was readily obtained, figure 5.4.1-2. For comparison, the complex $[PdMe_3(pz_3CH)]BF_4$ was also prepared, from $[PdMe_3(pz_3CH)]I$ and $AgBF_4$, and a spectrum of this complex in chloroform-D, figure 5.4.1-3, is similar to

that for $[PdMe_3(pz_3CH)]I$ and the platinum(IV) analogue $[PtMe_3(pz_3CH)]BF_4$.†

Figure 5.4.1-2. ^1H NMR of $[PdMe_3(pz_3CH)]I$ in Chloroform-D.



Following the successful isolation of $[PdMe_3(pz_3CH)]I$, a similar preparative method led to the isolation of palladium(IV) complexes containing the tridentate ligands pz_2mimCH, pz_2pyCH, py_3CH, py_2mimCH, and $pymim_2CH$. The complexes gave microanalyses and N.M.R. spectra (chloroform-D) consistent with the formulation $[PdMe_3(L_3)]I$, figures 5.4.1-4-8. For example, $[PdMe_3(py_3CH)]I$ displayed one ring environment and one Pd^{IV}-Me environment, while the mixed donor ligand complexes, *e.g.* $[PdMe_3(pz_2pyCH)I$, displayed two ligand environments and two Pd^{IV}-Me environments in 2:1 ratio.

† The complex $[PtMe_3(pz_3CH)]BF_4$ was prepared from reaction of $[PtMe_3I]_4$ and pz_3CH, followed by $AgBF_4$, following a similar procedure to that reported for synthesis of the hexafluorophosphate.[73]

Figure 5.4.1-3. ^1H NMR of $[PdMe_3(pz_3CH)]BF_4$ in Chloroform-D.

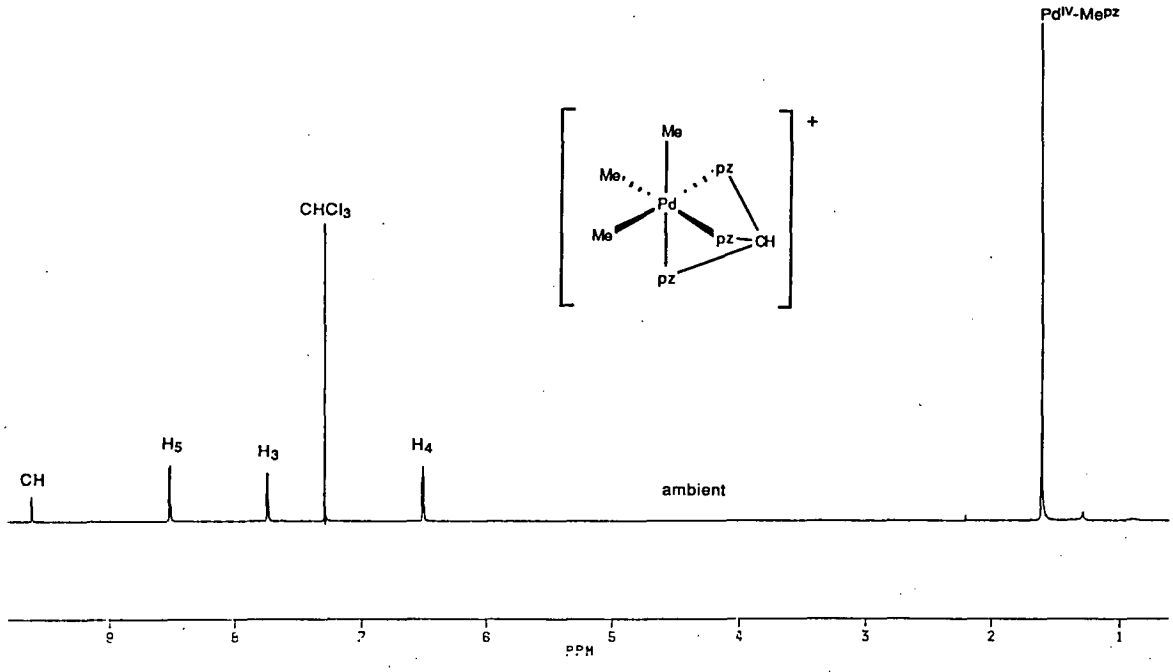


Figure 5.4.1-4. ^1H NMR of $[PdMe_3(py_3CH)]I$ in Chloroform-D.

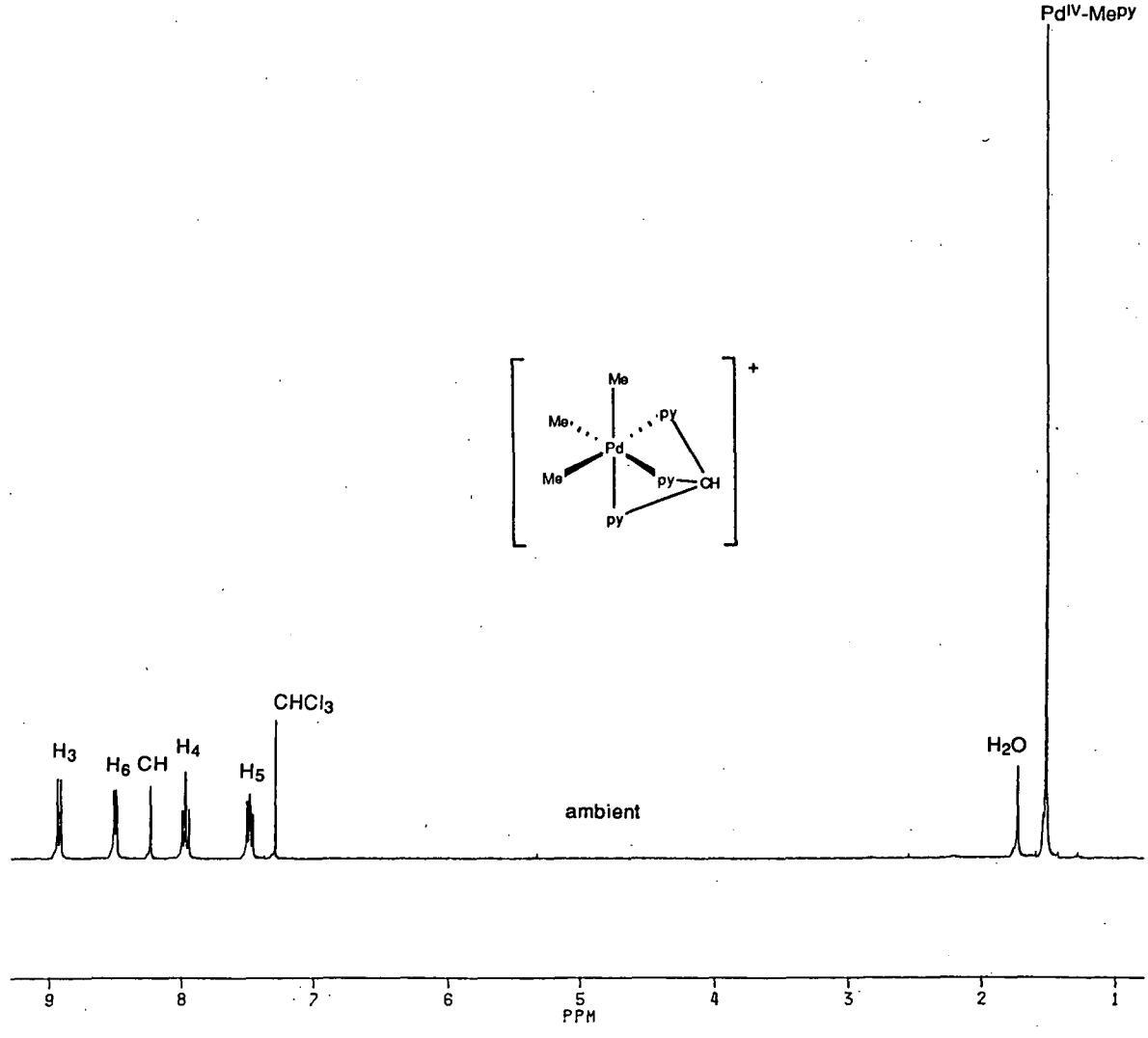


Figure 5.4.1-5. ^{1}H NMR of [PdMe$_3$(pz$_2$mimCH)]I in Chloroform-D.

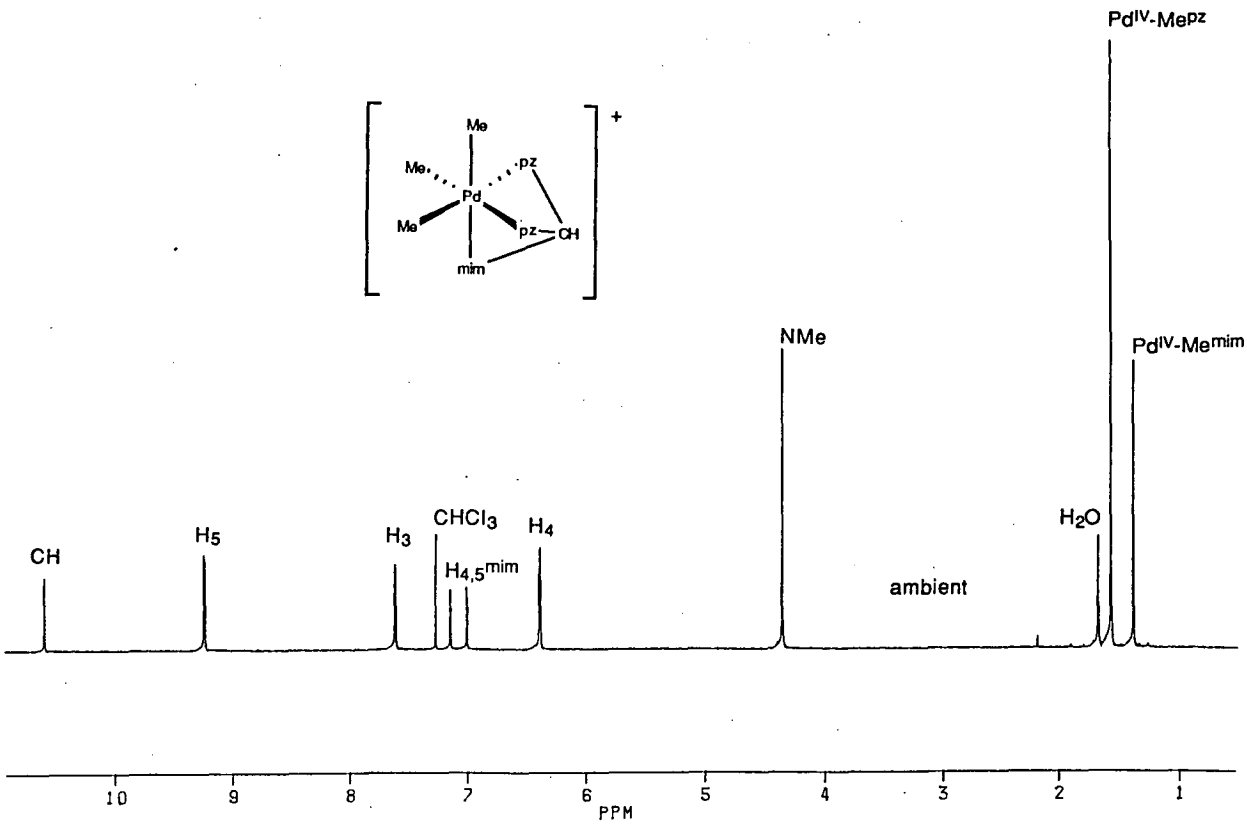


Figure 5.4.1-6. ^{1}H NMR of [PdMe$_3$(pz$_2$pyCH)]I in Chloroform-D.

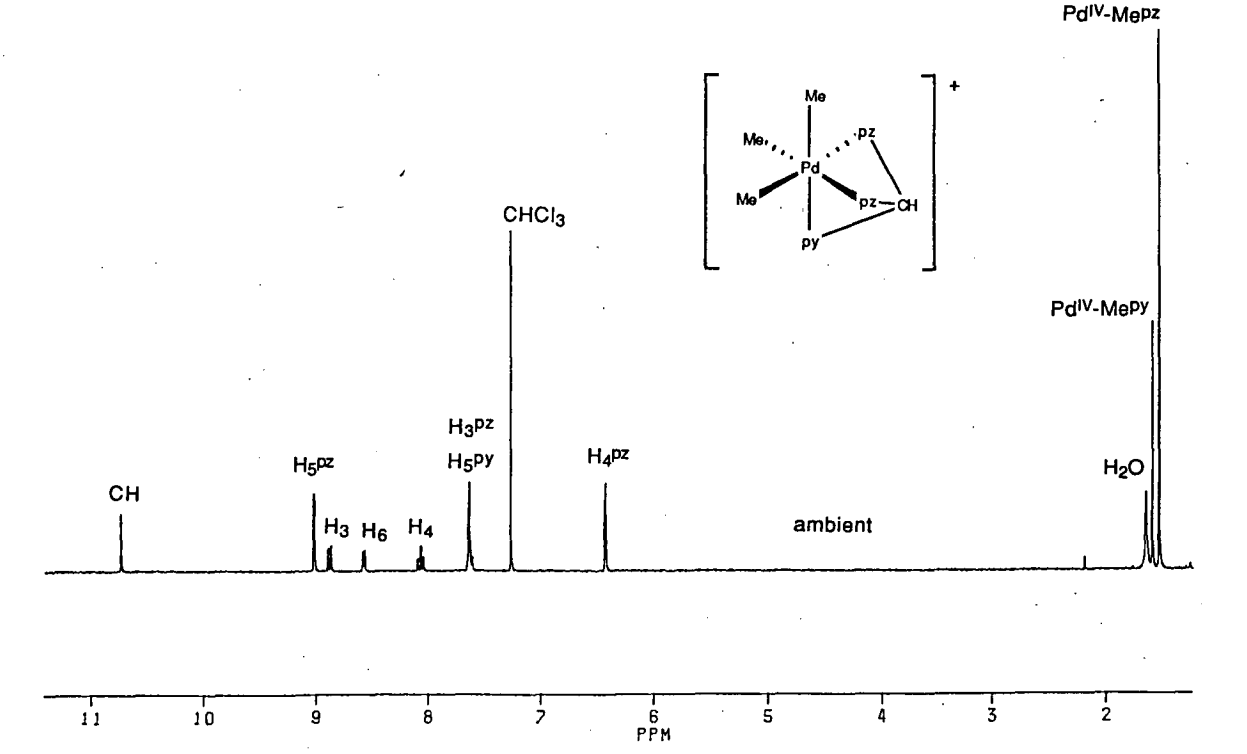


Figure 5.4.1-7. ^{1}H NMR of [PdMe$_3$(py$_2$mimCH)]I in Chloroform-D.

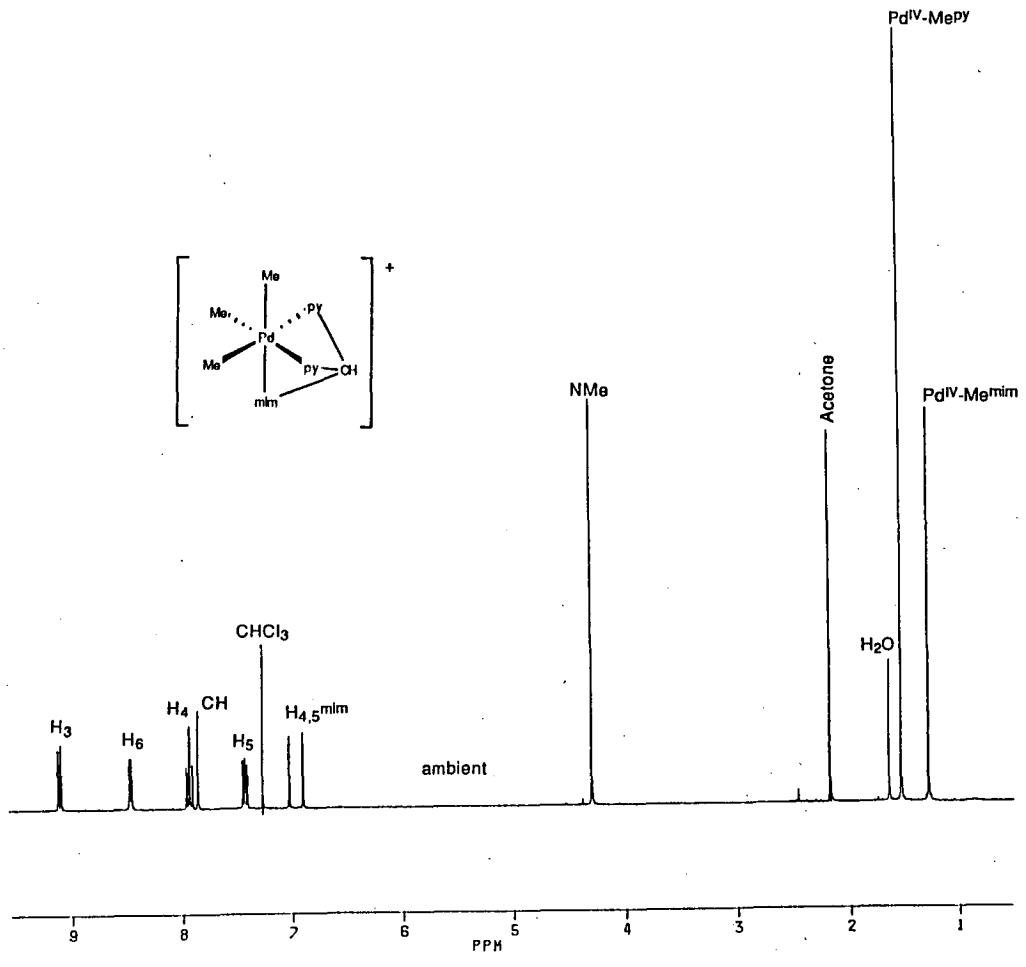
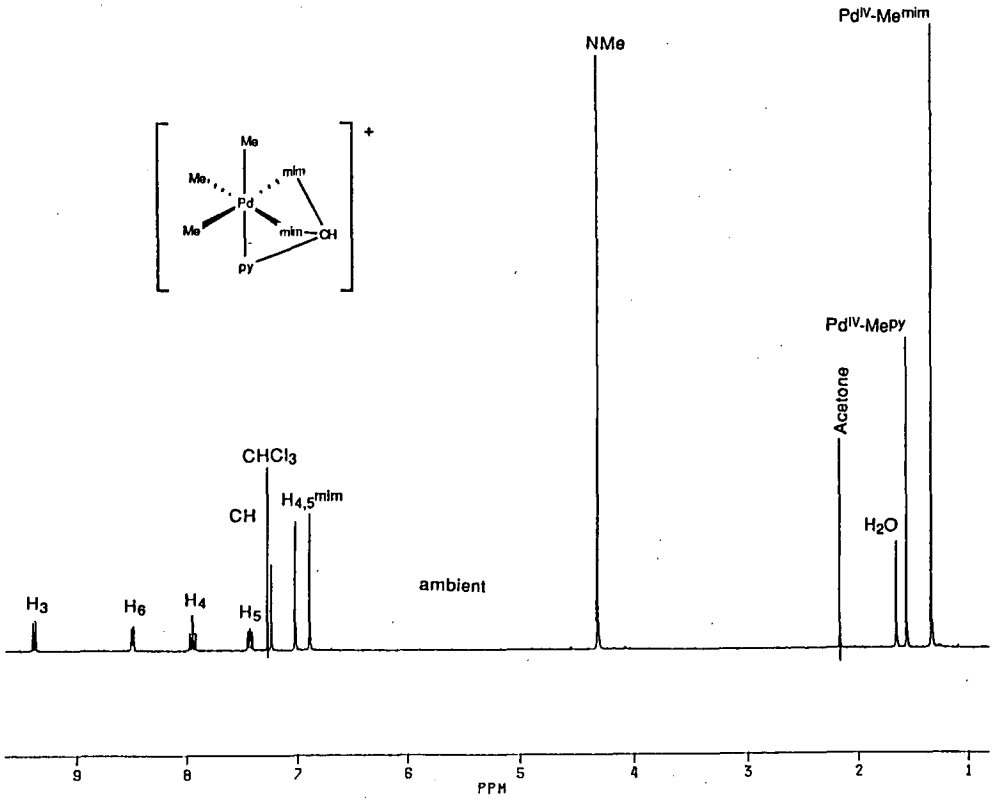


Figure 5.4.1-8. ^{1}H NMR of [PdMe$_3$(pymim$_2$CH)]I in Chloroform-D.



The complexes $[PdMe_3(L_3)]I$ exhibited remarkable stability, with only $[PdMe_3(pz_3CH)]I$ giving trace amounts of ethane and $\{PdMeI(pz_3CH)\}$ after 2-4 hours at ambient temperature. Indeed, $[PdMe_3(py_2mimCH)]I$ and $[PdMe_3(pymim_2CH)]I$ could be heated in chloroform for 1 hour at 60°C with no trace of reductive elimination evident. Solutions of $[PdMe_3(L_3)]I$ (L_3=pz_3CH, pz_2pyCH, pz_2mimCH) in deuterated solvents displayed a curious feature, deuteration of the bridgehead proton. For example, dissolution of $[PdMe_3(pz_3CH)]I$ in chloroform-D gave the expected integration values for **all** resonances, but after *ca.* 3 hours the bridgehead proton integrated for only ~30% of that expected, with a concomitant increase in the chloroform resonance. This process was reversible upon addition of chloroform to the residue obtained on removal of chloroform/chloroform-D.

5.4.2 Structure Determination of $[MMe_3(pz_3CH)]I$ (Me=Pd, Pt)

Crystals of the complex $[PdMe_3(pz_3CH)]I$ suitable for a structural study were obtained directly from a reaction between MeI and $\{PdMe_2(pz_3CH)\}$ under the conditions described above. For comparison, the structure of the platinum(IV) analogue $[PtMe_3(pz_3CH)]I$ was determined, and crystals of $[PtMe_3(pz_3CH)]I$ were obtained upon dissolution of the complex in acetone and slow vapour diffusion of diethyl ether at -20°C over 12 hours in a sealed chamber. The structures were determined by Dr. A. H. White and B. W. Skeleton of the University of Western Australia, and are displayed in figure 5.4.2-1; selected bond lengths and angles are listed in table 5.4.2-1.

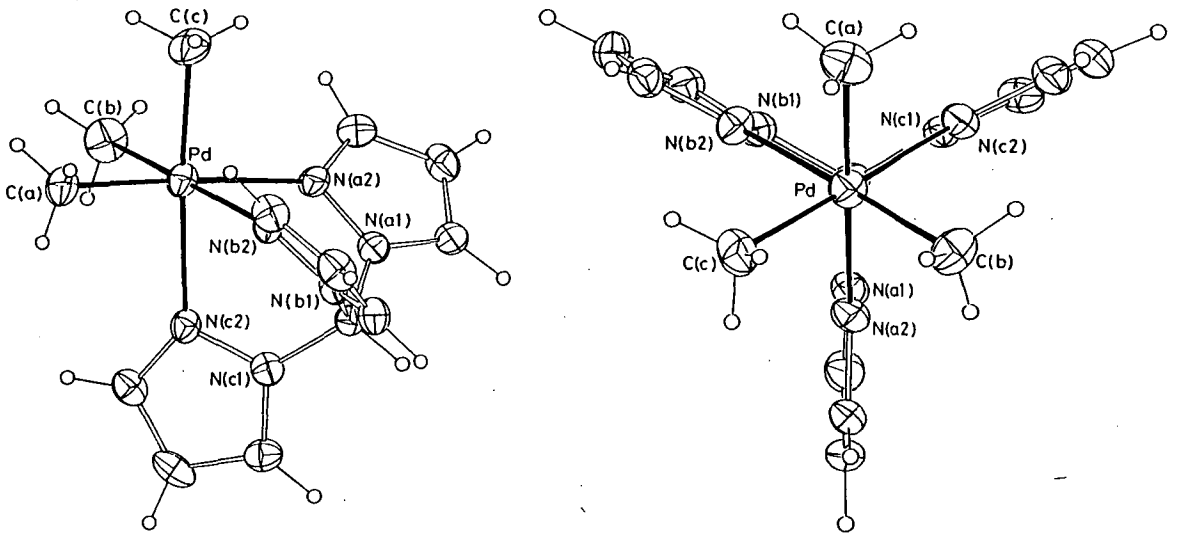
Crystals of $[MMe_3(pz_3CH)]I$ (M=Pd, Pt) are isomorphous, and the isostructural cations have octahedral '*fac*-MC_3N_3' geometry, with similar angles at Pd and Pt. The complexes have C-M-C angles 86.6(4)-88.0(4)° (Pd) and 87.9(3)-89.2(3)° (Pt), with smaller N-M-N angles owing to the 'bite' of tridentate pz_3CH, 81.7(3)-83.2(3)° (Pd) and 82.9(2)-84.1(2)° (Pt), resulting in slight distortion from an octahedral geometry.

Table 5.4.2-1. Coordination Geometry for the Palladium Atom in *fac*-[$MMe_3(pz_3CH)$]I distances in Å, angles in °

	Pd	Pt
	Bond Distances	
M-C(a)	2.036(11)	2.031(8)
M-C(b)	2.060(9)	2.056(7)
M-C(c)	2.049(10)	2.056(7)
M-N(a2)	2.191(8)	2.156(b)
M-N(b2)	2.207(7)	2.156(5)
M-N(c2)	2.225(7)	2.189(5)
	Bond Angles	
C(a)-M-C(b)	86.6(4)	87.9(3)
C(a)-M-C(c)	88.0(4)	89.2(3)
C(b)-M-C(c)	87.4(4)	88.4(3)
N(a2)-M-N(b2)	83.2(3)	84.1(2)
N(a2)-M-N(c2)	81.7(3)	83.0(2)
N(b2)-M-N(c2)	82.4(2)	83.7(2)
C(a)-M-N(a2)	176.8(3)	177.3(2)
C(a)-M-N(62)	95.1(3)	94.4(2)
C(a)-M-N(c2)	95.4(3)	94.6(2)
C(b)-M-N(a2)	95.0(3)	93.5(3)
C(b)-M-N(b2)	177.8(3)	176.9(3)
C(b)-M-N(c2)	96.1(3)	94.0(2)
C(c)-M-N(a2)	94.8(3)	93.2(3)
C(c)-M-N(b2)	94.1(3)	93.8(2)
C(c)-M-N(c2)	175.3(3)	175.6(3)
M-N(a2)-N(a1)	118.4(5)	117.1(4)
M-N(a2)-C(a3)	137.8(6)	136.3(5)
M-N(b2)-N(b1)	117.8(5)	117.9(3)
M-N(b2)-N(b3)	137.1(7)	137.0(5)
M-N(c2)-N(c1)	117.2(5)	116.3(3)
M-N(c2)-N(c3)	138.2(6)	138.3(5)

The pyrazol-1-yl rings are planar (χ^2 range from 0.3-2.3), with the Pd atom 0.084, 0.170, 0.119 Å from the mean planes of rings a,b,c respectively, and the Pt atom 0.036, 0.159, 0.078 Å from the corresponding planes.

Figure 5.4.2-1.



The M-C distances are essentially identical in both complexes, 2.04_8(Pd) and 2.04_8(Pt), but there is appreciable difference in the M-N distances, with that for the palladium complex being longer than that for platinum, 2.20_8 and 2.16_7Å respectively. A similar difference for M^{II}-P bond lengths in the isostructural palladium(II) and platinum(II) complexes *cis*-$\{MMe_2(PMePh_2)_2\}$ has been reported, with Pd-P 0.039(1) Å longer than Pt-P,[80] although in this instance Pd-C were appreciably shorter than Pt-C (~0.03Å).[80]

5.4.3 Mechanism for Reductive Elimination of Ethane from $[PdMe_3(L_3)]I$

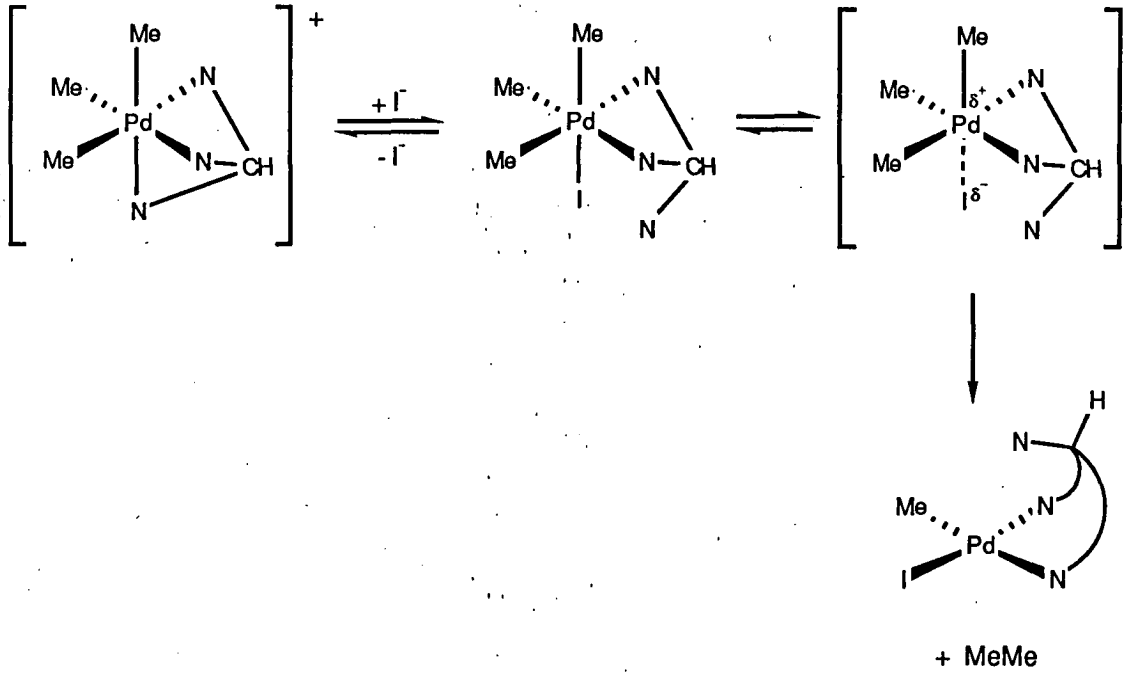
Kinetic studies of the reductive elimination of ethane from $\{PdMe_3I(bipy)\}$ suggest that the reaction involves at least partial ionisation of iodide, to form a polar species $[PdMe_3(bipy)^{\delta+}\cdots I^{\delta-}]$ or a tight ion pair $[Me_3(bipy)Pd]I$, prior to concerted elimination of ethane. However, the complexes $[PdMe_3(L_3)]I$, with **uncoordinated** iodide, are more stable than the bidentate ligand complexes $\{PdMe_3I(L_2)\}$ (L_2=bipy, phen). Further $[PdMe_3(pz_3CH)]BF_4$, prepared from $[PdMe_3(pz_3CH)]I$ and $AgBF_4$, failed to reductively eliminate ethane even after three days in chloroform-D at ambient temperature, conditions which result in complete reductive elimination of ethane from

[$PdMe_3(pz_3CH)$]I, and, in a similar experiment, [$PdMe_3(pz_3CH)$]BF_4 was found to be stable indefinitely in acetone-D6, but upon addition of a D_2O solution of KI reductive elimination of ethane commenced immediately.

These observations suggest that for the tridentate ligand complexes [$PdMe_3(L_3)$]I, coordination of iodide occurs to give the neutral species '$PdMe_3(L_3$-N,N')I' with a donor set identical to the neutral $Pd^{IV}Me_3$ complexes, prior to reductive elimination. Further, elimination of ethane from [$PdMe_3(pz_3CH)$]I was observed to proceed more rapidly in acetone-D6 than in chloroform-D (N.M.R.), in qualitative agreement with the kinetic studies for {$PdMe_3I(bipy)$} which determined that the reductive elimination proceeds more rapidly in polar solvents. The more polar solvents favour an ionic or polar intermediate.

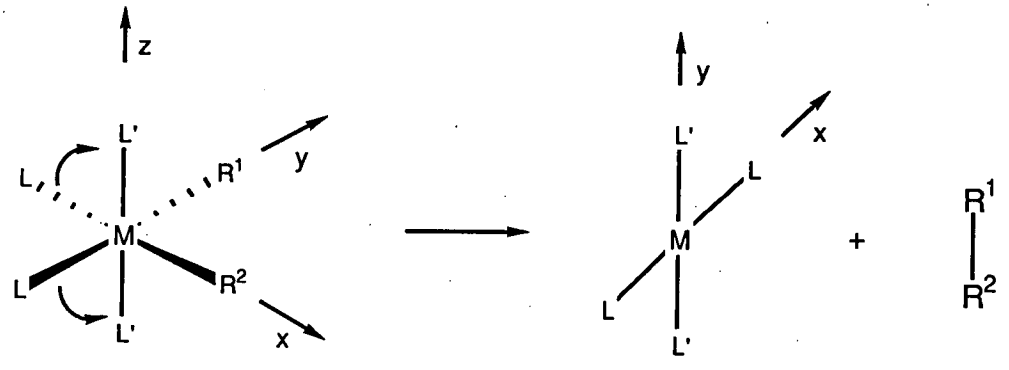
Thus, the proposed mechanism, scheme 5.4.3-1, consistent with the above observations and related kinetic studies for {$PdMe_3I(bipy)$}, involves coordination of iodide to form a neutral complex, followed by a reductive elimination of ethane. The participation of a polar intermediate rather than dissociated iodide is tentatively suggested.

Scheme 5.4.3-1.



The reductive elimination of ethane from [$PdMe_3(L_3)$]I *via* prior coordination of iodide, to give a neutral complex containing a bidentate ligand, is consistent with orbital symmetry correlation arguments.[81] For example scheme 5.4.3-2 represents an allowed process involving loss of R-R^1 with concomitant opening of the LML angle, and while this is not a symmetry requirement it must happen if the energy of the process is not to be raised.[81]

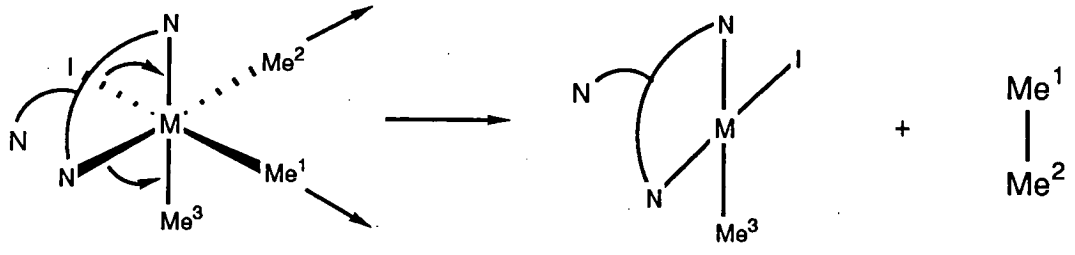
Scheme 5.4.3-2.



For [$PdMe_3(L_3)$]I, containing **tridentate** L_3, opening of the LML angle is not possible owing to constraints imposed by the ligand geometry. Coordination of iodide, however, results in the attainment of greater flexibility for the ligand, and allows reductive elimination to proceed without opening of the NMN angle. An important consequence of this approach is that alkyl groups *trans* to the bidentate ligand cannot reductively eliminate together, although this requirement may possibly be relaxed for more flexible bidentate ligands. Scheme 5.4.3-3 displays the reductive elimination of ethane from [$PdMe_3(pz_3CH)$]I, with ethane arising from coupling of the methyl group *trans* to iodide with another *trans* to pyrazole.

An identical scheme can be drawn for bidentate ligand complexes, so that these complexes do not require a re-arrangement of the type required for tripod ligand complexes.

Scheme 5.4.3-3.



5.4.4 Oxidative Addition Reactions with {$PdMe_2(pymim_2CH)$}

The stability of [$PdMe_3(pymim_2CH)$]I is remarkable with chloroform-D solutions exhibiting no trace of reductive elimination products after one hour at 60°C. Thus, the reaction of {$PdMe_2(pymim_2CH)$} with a variety of alkylhalides was investigated, with a view to increase the range of $Pd^{IV}Me_2R$ complexes. An *in situ* reaction between {$PdMe_2(pymim_2CH)$} and ethyl iodide, allyl bromide and benzyl bromide in acetone-D6 at ambient temperature immediately gave spectra exhibiting the formation of the palladium(IV) complexes [$PdMe_2R(pymim_2CH)$]X, and these complexes did not reductively eliminate ethane upon heating to 60°C. Subsequently, the palladium(IV) complexes [$PdMe_2R(pymim_2CH)$]X were prepared and isolated, from reaction between $\{PdMe_2(\mu\text{-pyd})\}_n$ and $pymim_2CH$ in acetone, followed by addition of RX and hexane.

The complexes exhibited poor to moderate solubility in acetone-D6 but were readily soluble in chloroform-D, and N.M.R. spectra obtained in this solvent are displayed in figures 5.4.4-1-3. The spectra show the presence of two isomers, A and B in figure 5.4.4-4, in similar ratios to that observed for the *in situ* reaction in acetone-D6, *viz ca.* 1:1 for [$PdMe_2(CH_2Ph)(pymim_2CH)$]Br, 5:3 for [$PdMe_2(Et)(pymim_2CH)$]I, and 6:5 for [$PdMe_2(allyl)(pymim_2CH)$]Br. Assignment of protons within each isomer (A,B) for the complexes is possible directly from integration and COSY spectra, and from the observation that isomer B gives inequivalent Pd-Me and *N*-methylimidazole resonances, and inequivalent $PdCH_2$ proton resonances owing to the chirality of the palladium centre. For

Figure 5.4.4-1. ^{1}H NMR of [PdMe$_2$Et(pymim$_2$CH)]I in Chloroform-D.

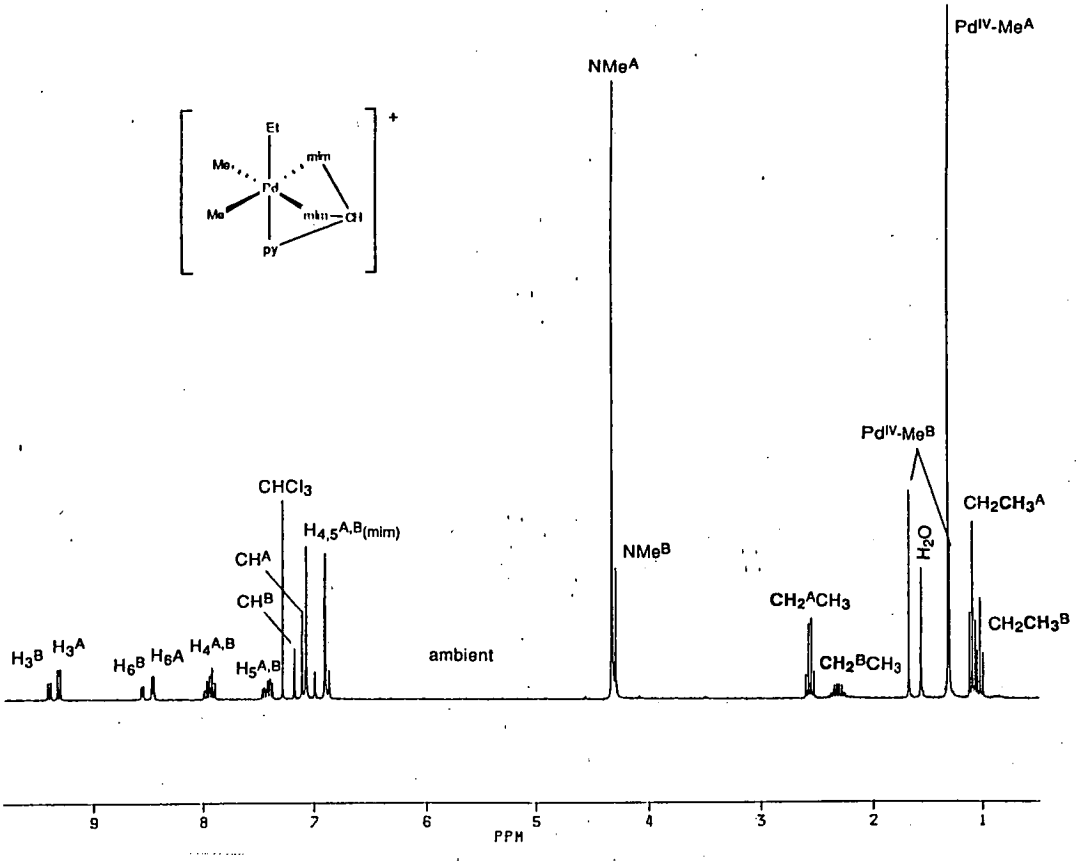


Figure 5.4.4-2. ^{1}H NMR of [PdMe$_2$(allyl)(pymim$_2$CH)]Br in Chloroform-D.

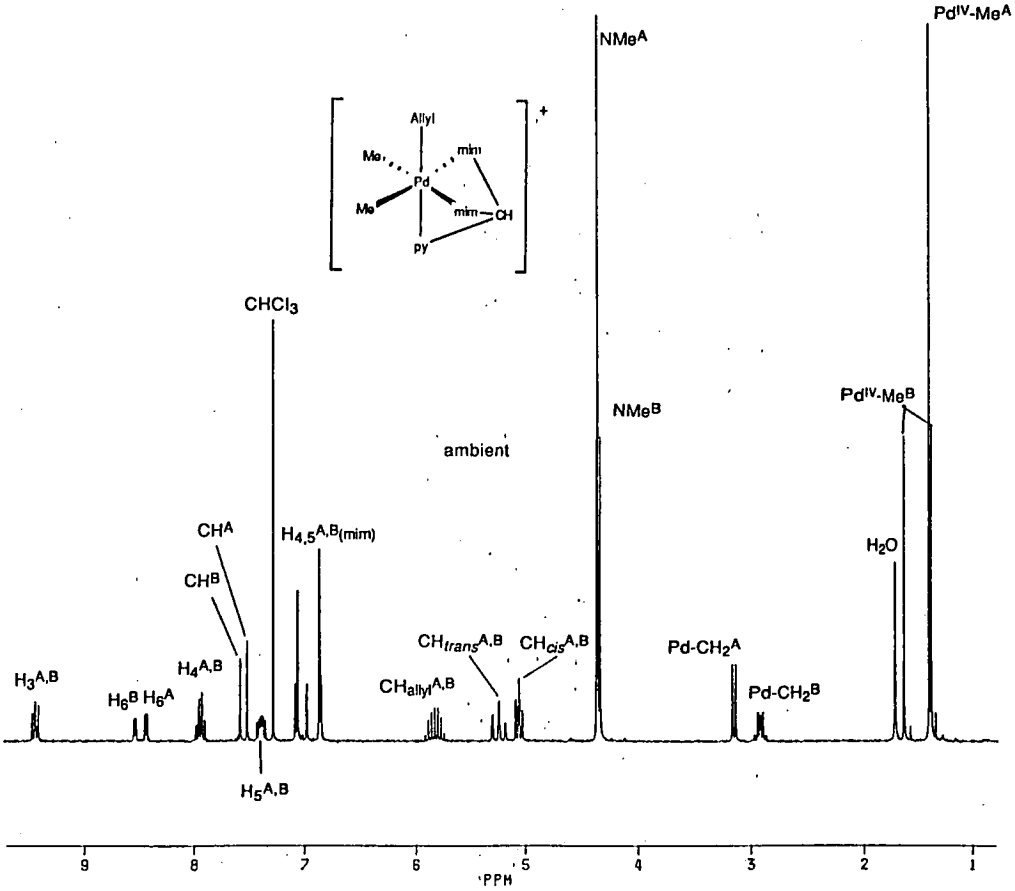
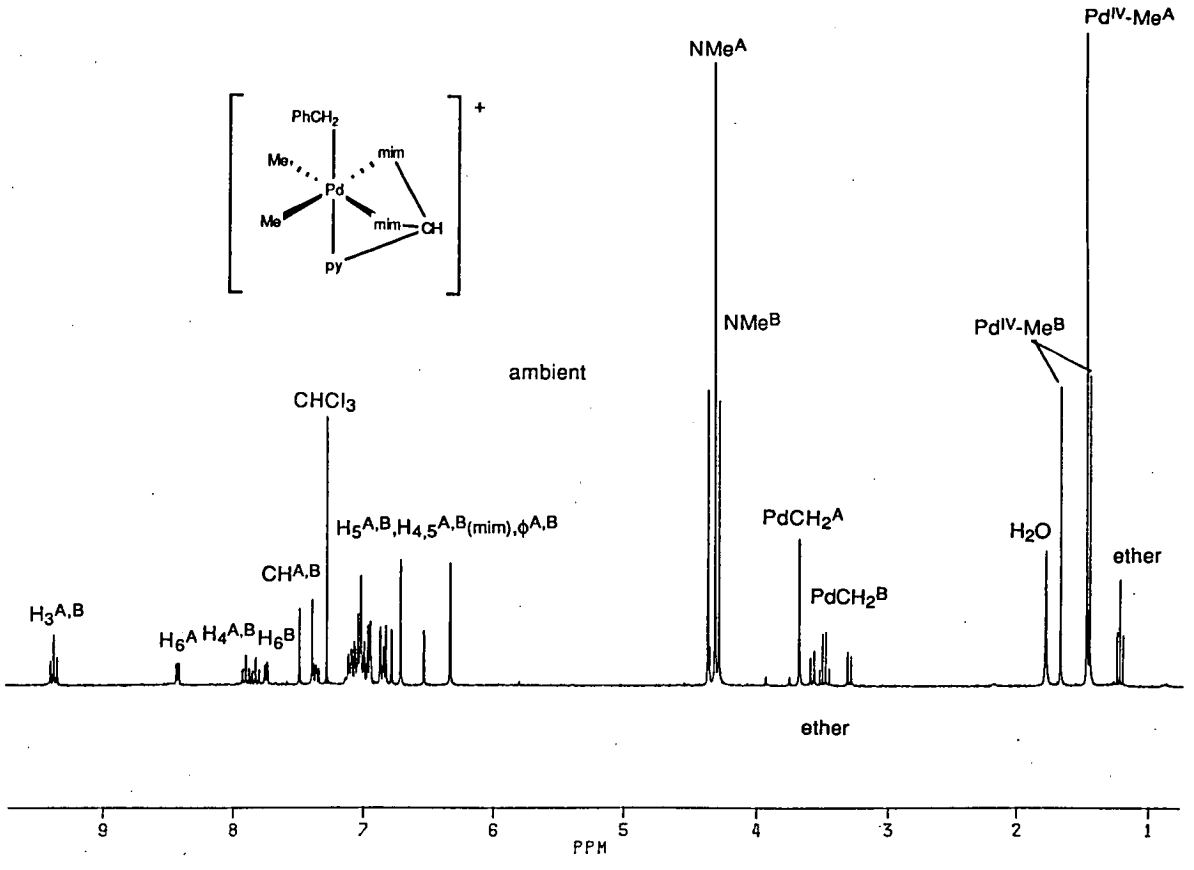


Figure 5.4.4-3. ^{1}H NMR of [PdMe$_2$(CH$_2$Ph)(pymim$_2$CH)]Br in Chloroform-D.



[PdMe$_2$(CH$_2$Ph)(pymim$_2$CH)]Br, which displays a 1:1 ratio of isomers A and B, support for the assignment shown is provided by the observation that H_6^B is shifted upfield (*ca.* 0.7 ppm) compared with H_6^A due to shielding by the adjacent benzyl group, an effect which would be absent in isomer A, figure 5.4.4-5.

Figure 5.4.4-5.

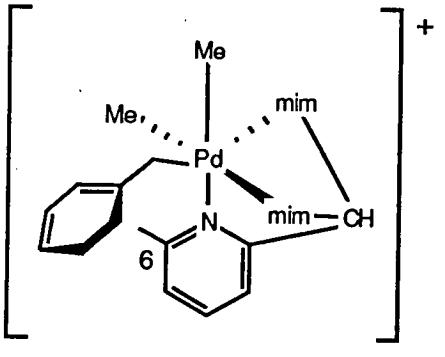
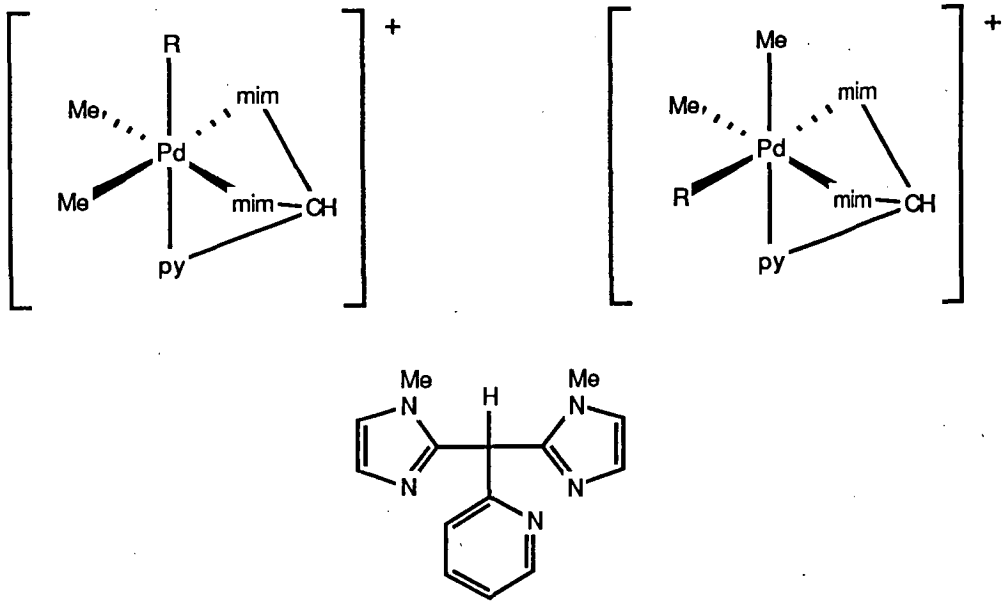


Figure 5.4.4-4.



5.5 LEAVING GROUP PREFERENCES FOR {$PdMe_2$(bipy)} COMPLEXES

In an earlier section it was noted that oxidative addition of CD_3I to {$PdMe_2$(bipy)} gave MeMe and $MeCD_3$ in *ca.* 1:1 ratio, but based on a statistical approach a ratio of 1:2 (MeMe:$MeCD_3$) is predicted. A similar effect has been noted for reductive elimination of ethane from {$PtMe_2(CD_3)(PMe_2Ph)_2$}.[71] This result suggests that CH_3 groups are eliminated preferentially from {$PdMe_2(CD_3)I$(bipy)}, because oxidative addition of CD_3I to {$PdMe_2$(bipy)} at -60°C gives a spectrum showing scrambling of CD_3 and Me groups has occurred, prior to warming the solution to study the reductive elimination process. To further investigate the ease of elimination of different alkyl groups, oxidative addition of EtI, CH_2=$CHCH_2Br$, and $PhCH_2Br$ to {$PdMe_2$(bipy)} was investigated.

Similar studies were also carried out for {$PdMe_2(pz_2CMe_2)$}, since this complex forms an unstable Pd(IV) complex with MeI, and palladium(II) complexes of pz_2CMe_2 are generally very soluble, in contrast to bipy complexes which are frequently insoluble. Although a direct comparison between results for these complexes requires caution, because the structure of the MeI oxidative addition product

for {$PdMe_2(pz_2CMe_2)$} has not been established, the high solubility and ease of reductive elimination provide convenient experimental conditions.

Oxidative addition of EtI to {$PdMe_2(bipy)$} occurred slowly at ambient temperature, with complete reaction of {$PdMe_2(bipy)$} requiring 2-3 hours. The reaction gave {PdMeI(bipy)} and {PdEtI(bipy)} in *ca.* 1:1 ratio, figure 5.5-1e, and the gases ethane and propane could be removed upon purging the solution with N_2, figure 5.5-2. The appearance of these products provides compelling evidence for palladium(IV) intermediacy, and indeed bipy resonances attributable to a palladium(IV) intermediate were detected, figure 5.5-1c, although resonances arising from Pd^{IV}-Me and Pd^{IV}-Et groups could not be discerned.

Figure 5.5-1. ^1H NMR of {$PdMe_2(bipy)$} + EtI in Acetone-D6.

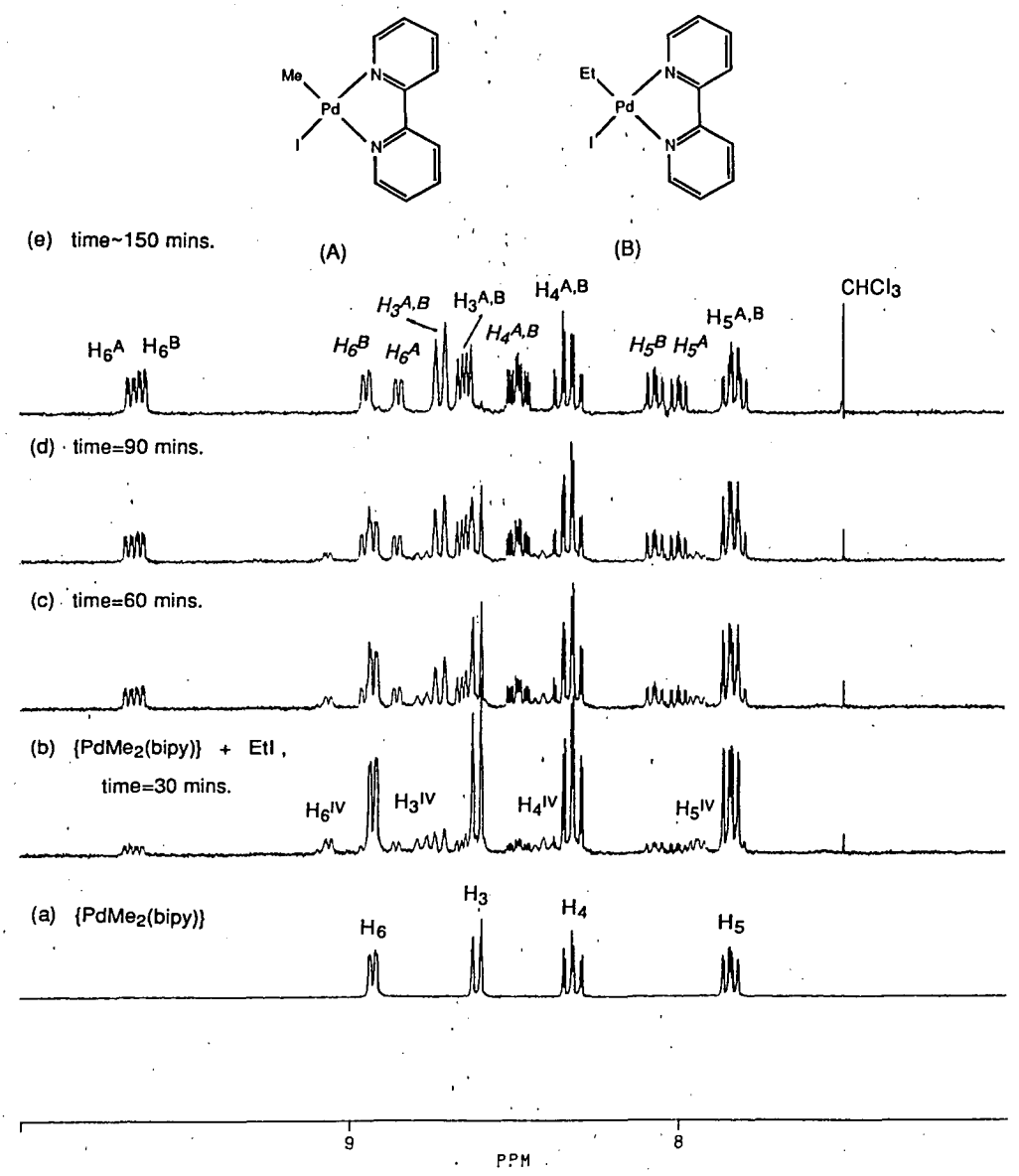
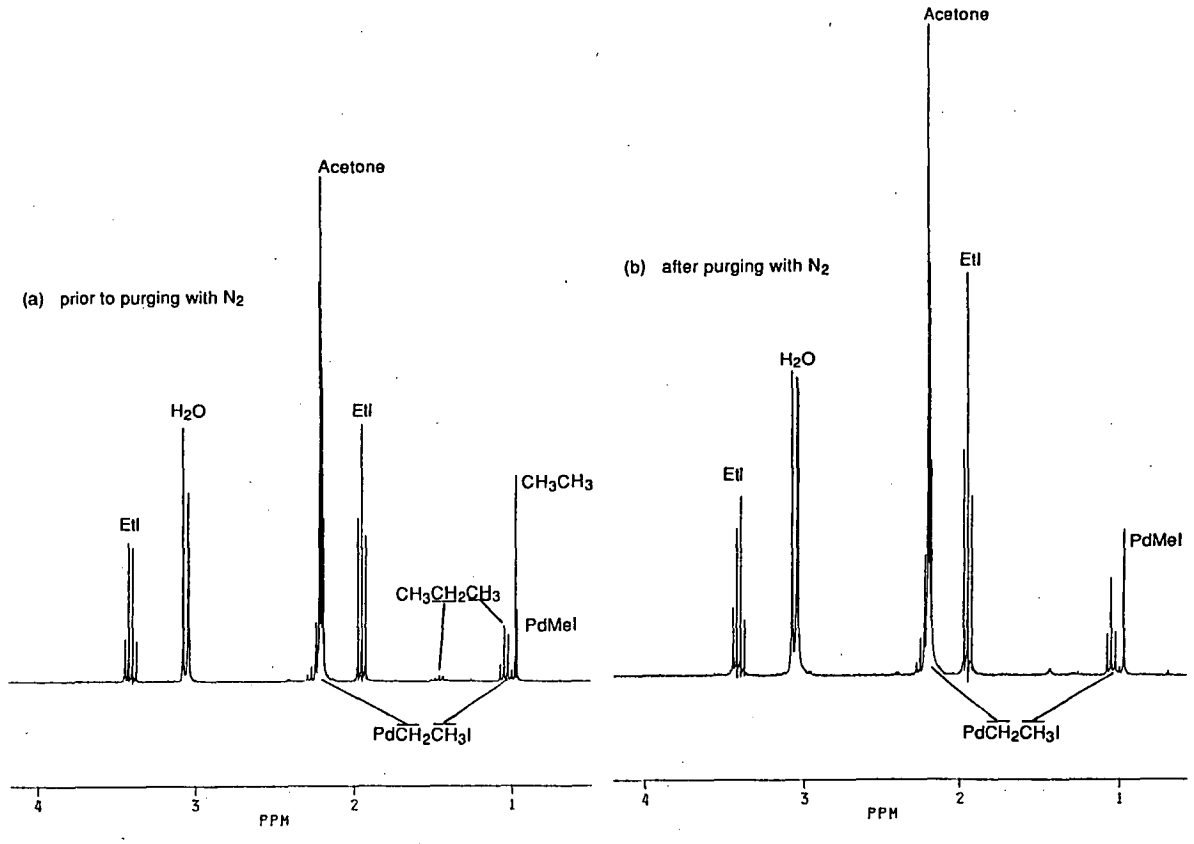


Figure 5.5-2. ^1H NMR of {$PdMe_2(bipy)$} + EtI in Acetone-D6.



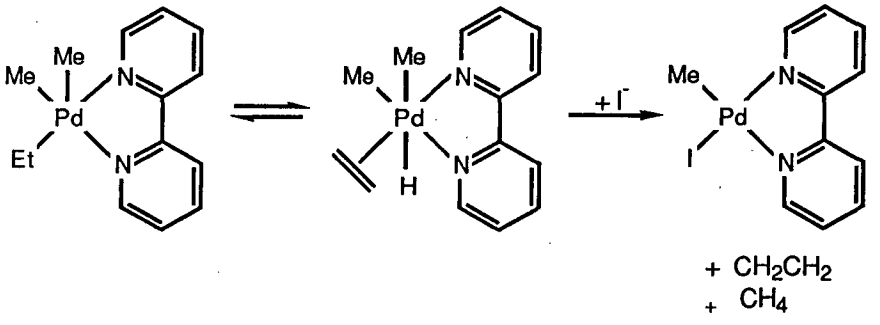
Spectra also displayed a sharp singlet at 5.38 ppm which grew in intensity with time, and could be removed upon purging with N_2. The appearance of this resonance coincided with the deposition of palladium metal, and based on this the gas has been assigned as ethene† , arising from β-hydrogen elimination. The appearance of ethene only towards the end of the oxidative addition reaction suggests that β-hydrogen elimination occurs from {PdEtI(bipy)} and not the Pd(IV) intermediate.

The complex {$PdMe_2(pz_2CMe_2)$} reacted slowly with EtI to produce {$PdMeI(pz_2CMe_2)$} and free pz_2CMe_2 in *ca.* 1:1 ratio, together with ethene (and Pd metal), ethane and methane (at 0.17 ppm†) with the removal of these gaseous products possible upon purging with N_2. Two possible pathways for the formation of methane

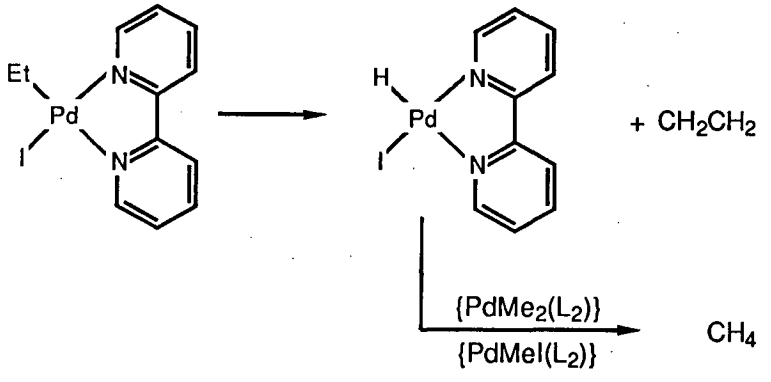
† An authentic sample of ethene gas in acetone-D6 exhibits an identical resonance.

† An authentic sample of methane gas in acetone-D6 has a resonance at 0.17 ppm.

are considered here, the first involving β-hydrogen elimination from a palladium(IV) intermediate, equation 5.5-1, and the second an intermolecular process, equation 5.5-2. Although either pathway is possible the latter is favoured as coupling to produce methane in the former could occur but would not explain the high yield of free ligand and palladium metal.



5.5-1

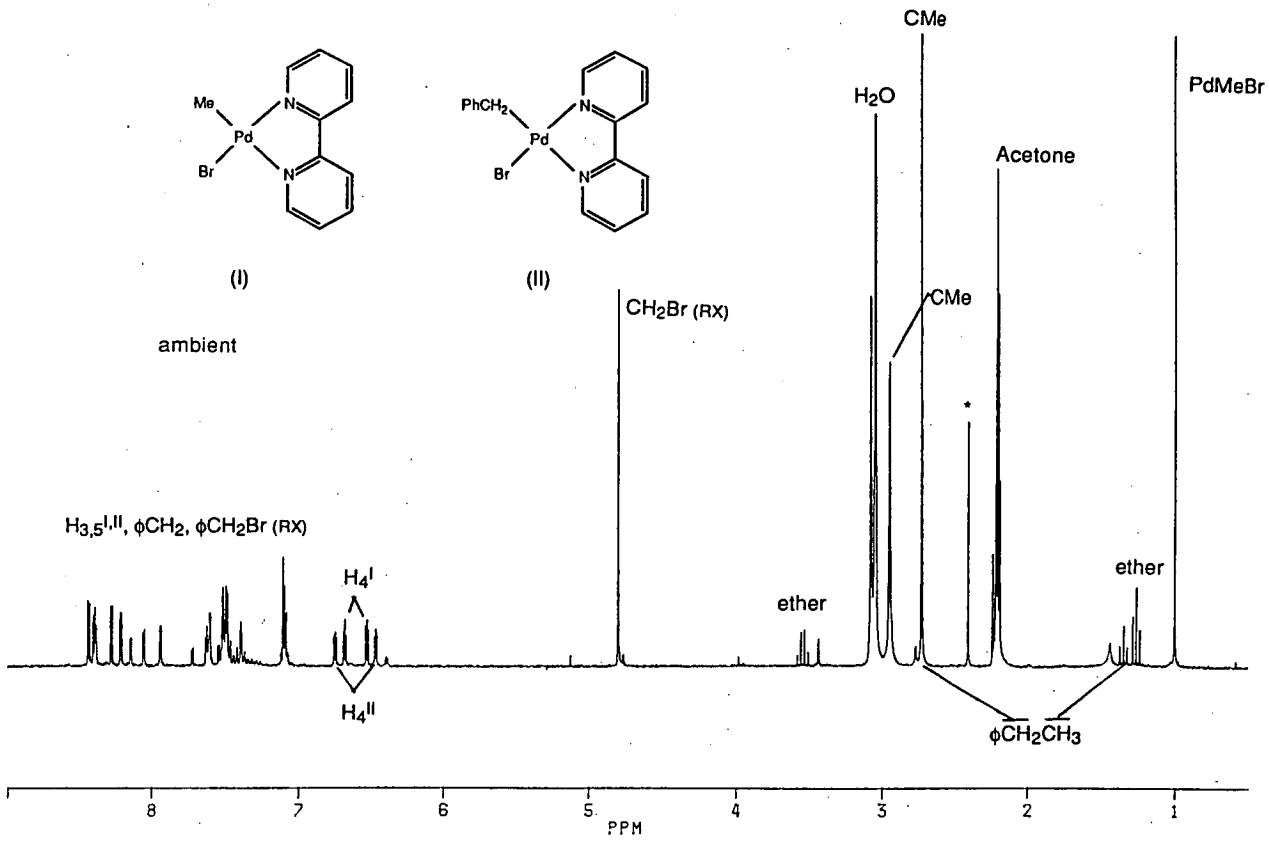


5.5-2

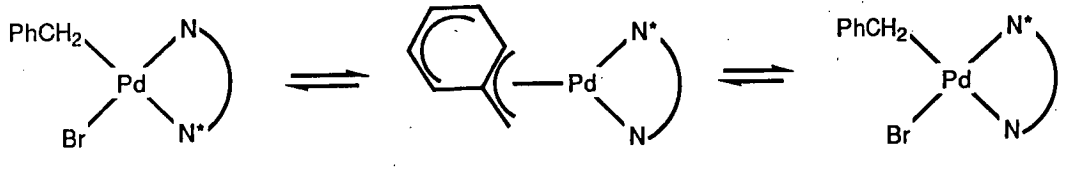
Oxidative addition of $PhCH_2Br$ to $\{PdMe_2(bipy)\}$ to form the stable isolable complex $\{PdMe_2(PhCH_2)Br(bipy)\}$ has been discussed, and it has been noted that reductive elimination from this complex occurs to produce ethane and $\{Pd(CH_2Ph)Br(bipy)\}$ as the major products (>90%). An analogous reaction with $\{PdMe_2(pz_2CMe_2)\}$ gave complex spectra which could not be assigned. However, a spectrum obtained after the reaction was complete showed the presence of $\{PdMeI(pz_2CMe_2)\}$, ethyl benzene and ethane, thus providing convincing evidence for Pd(IV) intermediacy.

The spectrum, figure 5.5-3, also showed the presence of a second palladium(II) product which, based on the formation of ethane, is expected to contain a benzyl group. On cooling the H_4^{II} resonances sharpened, and a pair of doublets (4.04

Figure 5.5-3. ^{1}H NMR of {$PdMe_2(pz_2CMe_2)$} + $PhCH_2Br$ in Acetone-D6.



and 2.80 ppm) could be discerned, and were assigned to the benzylic methylene protons. Warming resulted in broadening and coalescence of the H_4^{II} protons and the benzylic methylene protons to give broad resonances. This behaviour is consistent with exchange of the inequivalent benzylic protons, most readily accounted for by a $\sigma \rightarrow \Pi \rightarrow \sigma$ re-arrangement.



(II) (II)

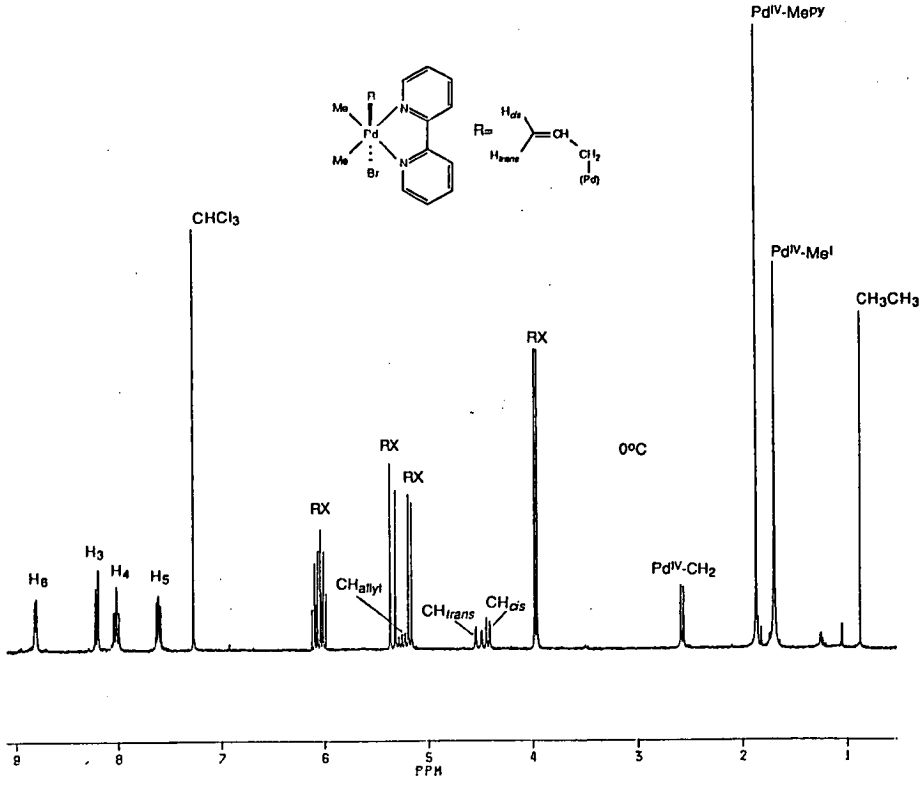
Allyl bromide oxidatively added to {$PdMe_2$(bipy)} at ambient temperature to produce a spectrum which displayed trace amounts of a palladium(IV) intermediate, together with ethane and {PdMeBr(bipy)}. An insoluble solid of analytical composition Pd(allyl)Br(bipy)† was also formed, and the palladium(II) products {PdMeBr(bipy)} and Pd(allyl)Br(bipy) were produced in *ca.* 1:5 ratio. Repeating this experiment at low temperature (0°C) gave a spectrum exhibiting a high yield of the palladium(IV) complex together with palladium(II) complexes. However, in chloroform-D, an identical experiment at 0°C gave a spectrum exhibiting only the palladium(IV) complex {$PdMe_2$(allyl)Br(bipy)} and a small amount of ethane, figure 5.5-5.

Chemical Shift Data for {$PdMe_2$(allyl)Br(bipy)} in Chloroform-D

bipy : 8.66 (H_6), 8.07 (H_3), 7.88 (H_4), 7.47 (H_5)

allyl : 5.11 (CH), 4.37 (CH_{trans}, ^3J=16.89 Hz), 4.29 (CH_{cis},^3J=9.78 Hz),

Pd^{IV}-R : 5.02 (-CH_2CHCH_2, ^3J=8.55 Hz), 1.73 (-CH_3)



† The complex Pd(allyl)Br(bipy) is too insoluble for NMR characterisation, and probably has the structure [(η^3-allyl)Pd(bipy)]Br in view of the proposal that the insoluble chloro-analogue has this structure.[82]

A similar *in situ* reaction between {$PdMe_2(pz_2CMe_2)$} and allyl bromide in acetone-D6 at ambient temperature did not produce a detectable palladium(IV) intermediate, but gave ethane, {$PdMeBr(pz_2CMe_2)$} and an allyl palladium(II) complex, with the palladium(II) products formed in *ca.* 1:10 ratio respectively, figure 5.5-6. The broadness of the aromatic and allylic resonances prompted a variable temperature study of this system. The complexity of the spectrum at -80°C (figure 5.5-7) was surprising, and to aid in its elucidation the allyl palladium(II) product was prepared and isolated from a larger scale reaction of {$PdMe_2(pz_2CMe_2)$} and allyl bromide, and for comparison a sample of this complex was converted to the BF_4^- salt. Although the BF_4^- salt analyzed correctly for $[Pd(allyl)(pz_2CMe_2)]BF_4$, the solid isolated from the oxidative addition reaction gave a microanalysis suggesting the empirical formula '$Pd(allyl)_2Br_2(pz_2CMe_2)$'. The discussion of these complexes commences with the BF_4^- salt, followed by the isolated bromo-complex and interpretation of the spectra obtained from the *in situ* reaction.

The tetrafluoroborate salt gave a sharp spectrum at ambient temperature indicating the presence of an η^3-allyl group and a single pyrazole ring environment, figure 5.5-8, thus suggesting the formulation $[Pd(\eta^3\text{-allyl})(pz_2CMe_2)]BF_4$. Cooling resulted in gradual broadening and separation of resonances to give, at -70°C, a spectrum showing the presence of two species in *ca.* 5:3 ratio, figure 5.5-9. This behaviour is consistent with boat to boat interconversion of the chelate ring. Further, as an η^3-allyl group does not lie in the plane of the metal, but in a plane nearly perpendicular to it, conformer A is expected to exhibit greater allyl···CMe(ligand) interactions that conformer B, leading to the tentative assignment of conformer B as the major product to minimise steric interactions.

The ambient temperature N.M.R. spectrum of the isolated bromo-complex exhibits broad resonances, and the complex is clearly fluxional, figure 5.5-10. Cooling to -70°C gave a complex spectrum, figure 5.5-11, exhibiting resonances identical to that observed for $[Pd(\eta^3\text{-allyl})Br(pz_2CMe_2)]BF_4$ at low temperature (including an identical conformer ratio of 5:3), together with an equal amount of another η^3-allyl species. Based on microanalytical results, and the presence of [Pd(η^3-

allyl)Br(pz_2CMe_2)]$^+$, the anion is formulated as [Pd(η^3-allyl)Br_2]$^-$, and in support of this the η^3-allyl group has similar resonance positions to that reported for the closely related complex [Pd(η^3-allyl)Br_2][PPh_4].[83] A structural study of a similar complex containing the cation/anion pair [Pd(η^3-butenyl)(tmeda)][Pd(η^3-butenyl)Cl_2] has been reported recently.[84]

Returning briefly to the *in situ* experiment, the low temperature limiting spectrum displayed in 5.5-7 clearly exhibits resonances attributable to the complex [Pd(η^3-allyl)(pz_2CMe_2)][Pd(η^3-allyl)Br_2], together with resonances arising from free pz_2CMe_2, and at higher temperatures rapid ligand exchange occurs. Indeed, reaction of isolated [Pd(η^3-allyl)(pz_2CMe_2)][Pd(η^3-allyl)Br_2] with one mole equivalent of free ligand gave identical N.M.R. spectra to that observed from an *in situ* reaction.

Figure 5.5-6. ^{1}H NMR of {$PdMe_2(pz_2CMe_2)$} + allylbromide in Acetone-D6.

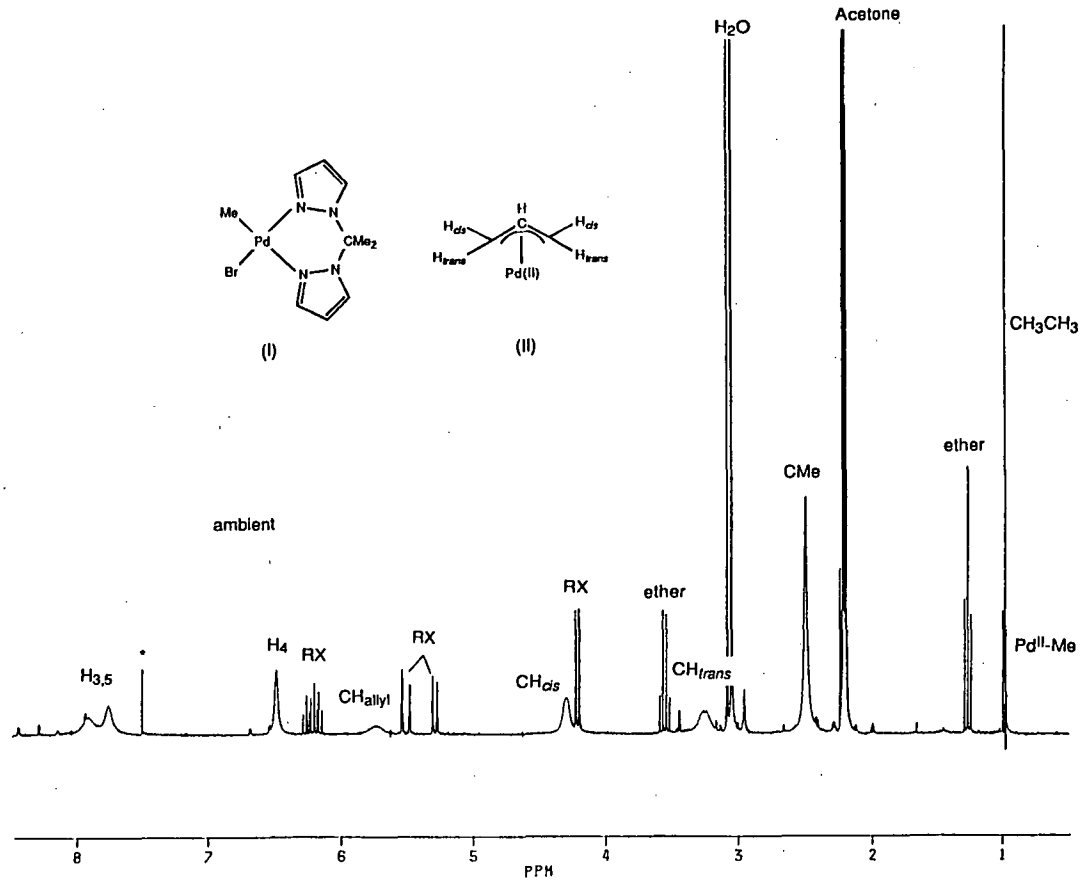


Figure 5.5-7. ^{1}H NMR of {$PdMe_2(pz_2CMe_2)$} + allylbromide in Acetone-D6.

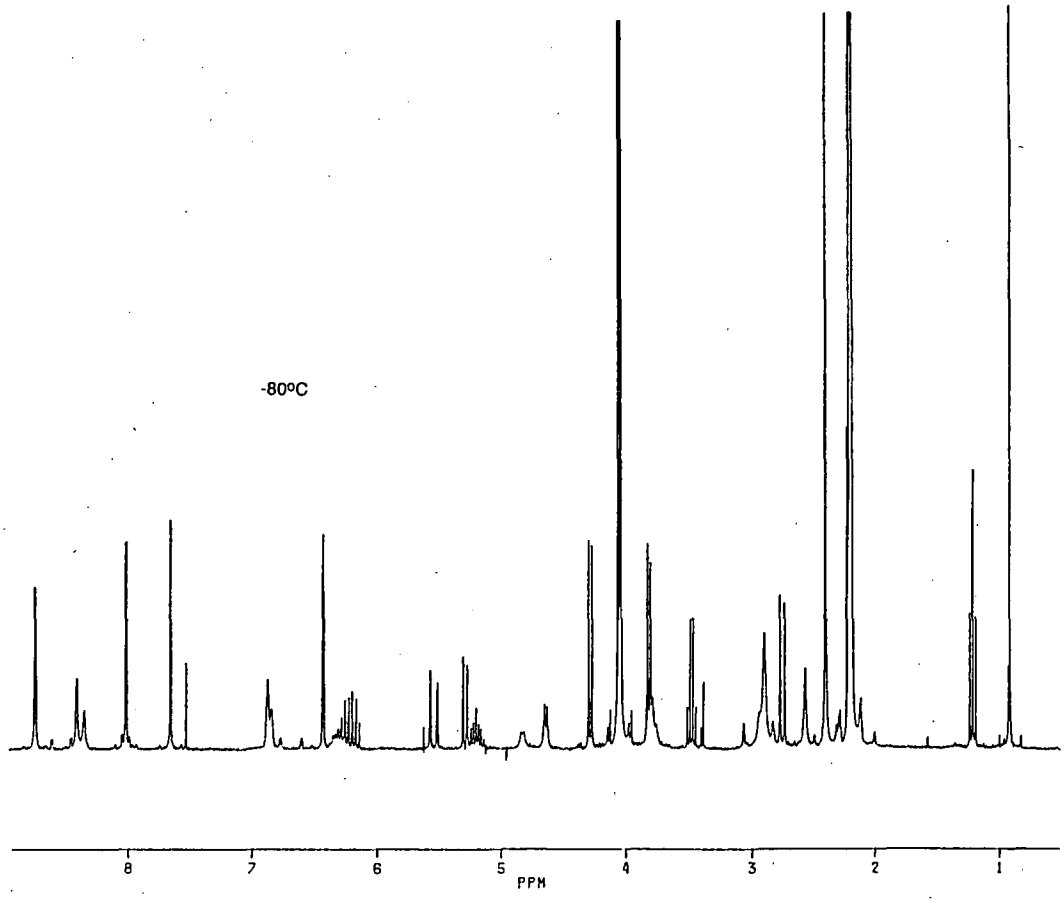


Figure 5.5-8. ^1H NMR of $[(\eta^3\text{-allyl})Pd(pz_2CMe_2)]BF_4$ in Acetone-D6.

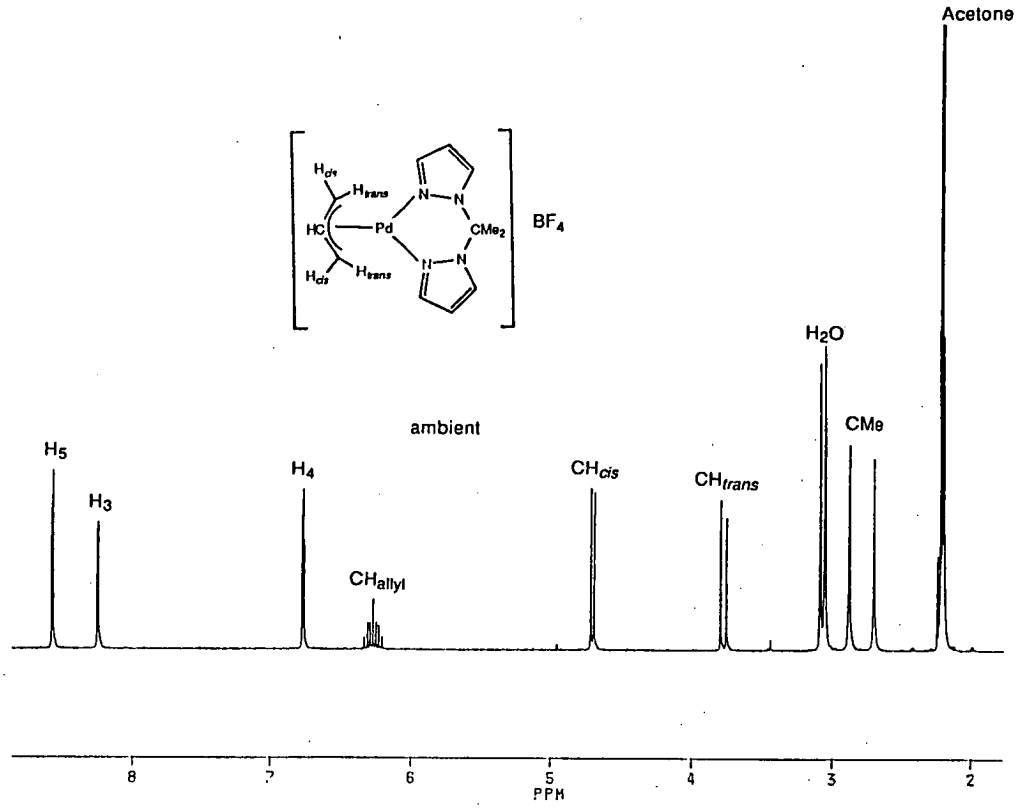


Figure 5.5-9. ^1H NMR of $[(\eta^3\text{-allyl})Pd(pz_2CMe_2)]BF_4$ in Acetone-D6.

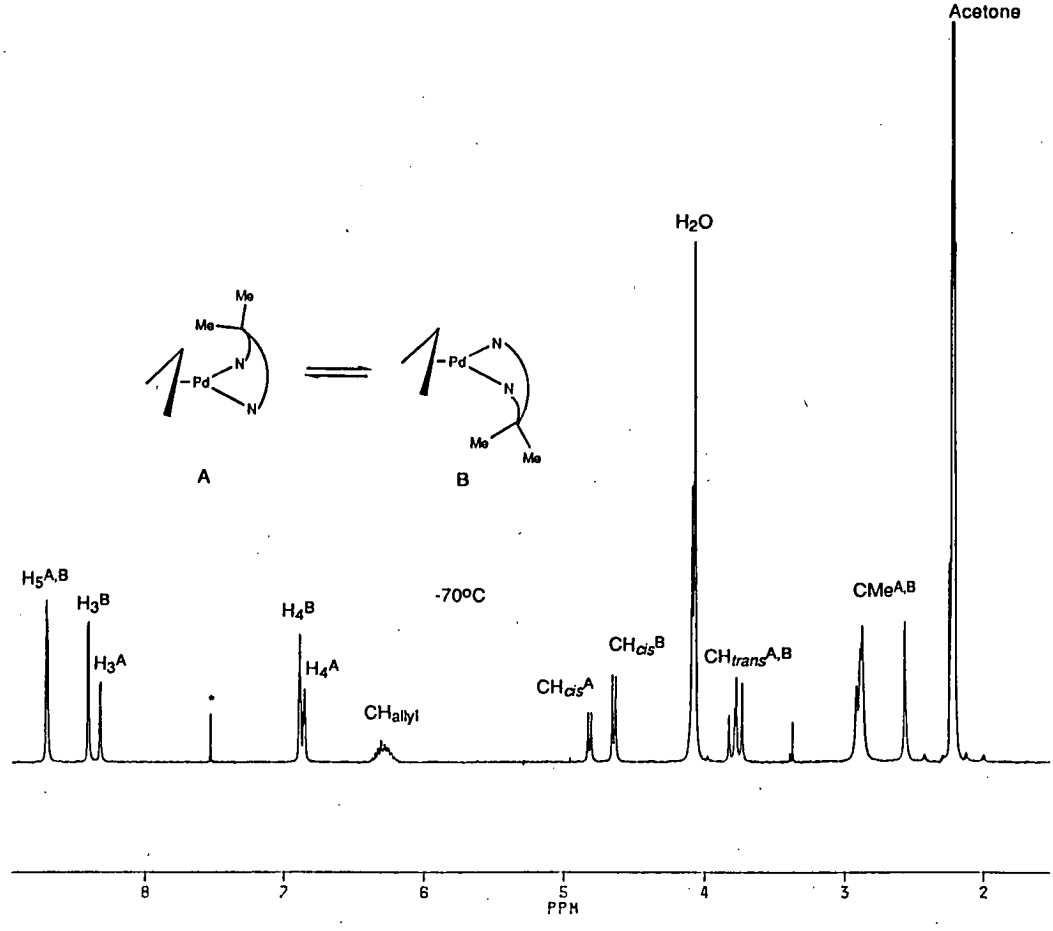


Figure 5.5-10. ^{1}H NMR of {$PdMe_2(pz_2CMe_2)$} + allylbromide (isolated) in Acetone-D6.

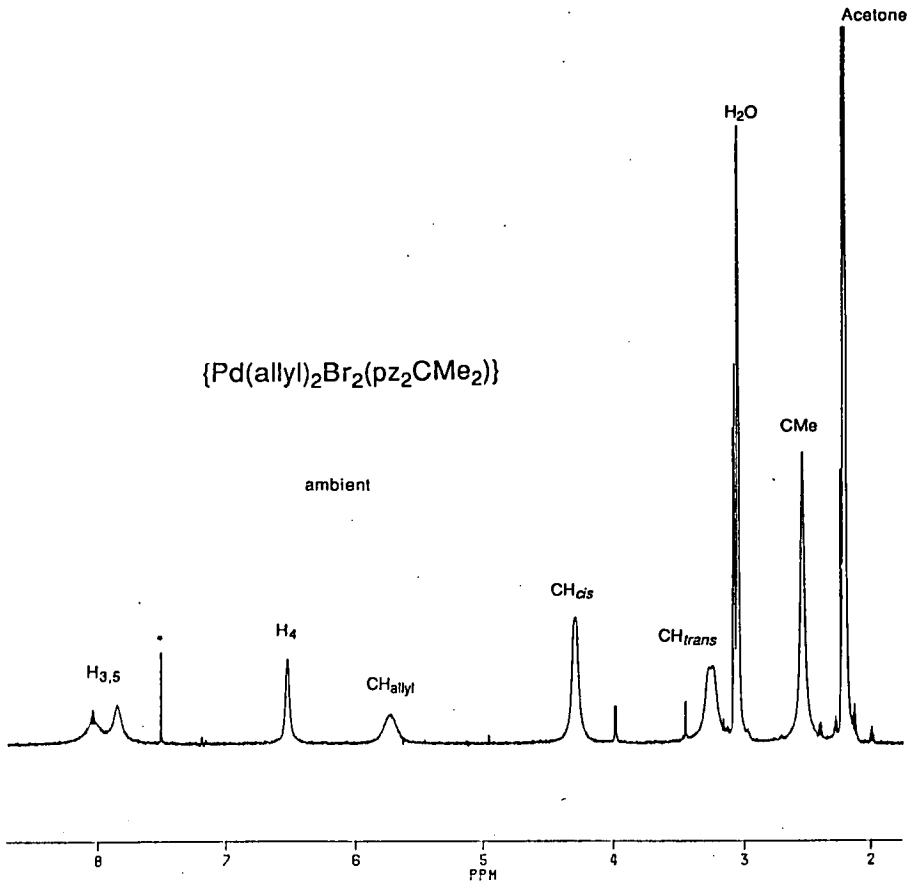
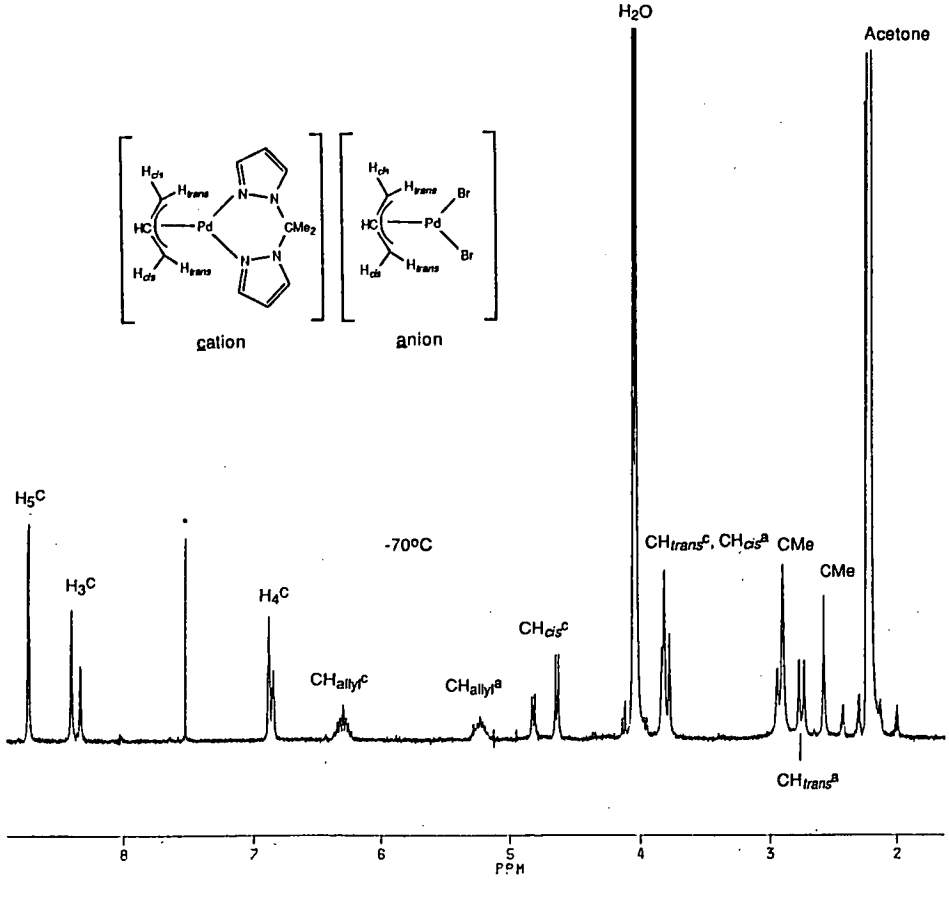


Figure 5.5-11. ^{1}H NMR of {$PdMe_2(pz_2CMe_2)$} + allylbromide (isolated) in Acetone-D6.

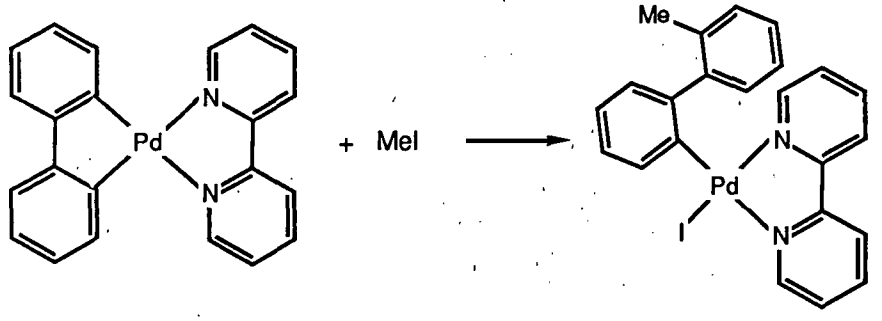


5.6 RECENT REPORTS OF Pd(IV) INTERMEDIATES

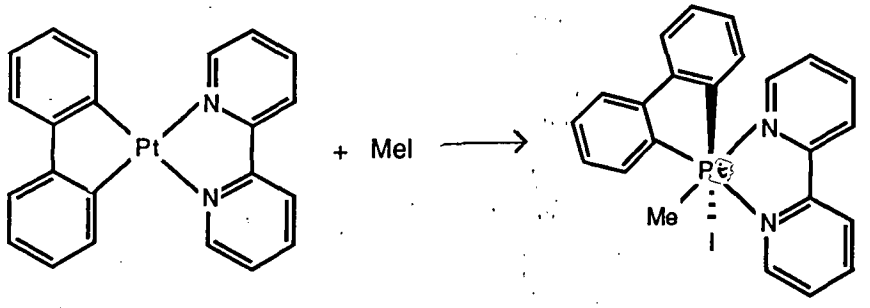
Following the publication of results arising from this study[85] several reports have appeared in the literature proposing the intermediacy of palladium(IV) complexes in stoichiometric and catalytic reactions.[86-89] In two instances the intermediate was detected from an *in situ* N.M.R. reaction,[88,89] and for one of these a solid was isolated.[89]

Kurosawa *et. al.*[86] have, as in an earlier paper,[68] reported the accelerating effect that added allyl halides have on the rate and distribution of reductive elimination products aryl-allyl and aryl-allyl' from (η^3-allyl')(aryl)palladium(II) complexes. These effects have been invoked as evidence for palladium(IV) intermediacy, although no structure(s) for the palladium(IV) intermediate was proposed.

Cornioley-Deuschel and von Zelewsky[87] reacted the complex {Pd(biph)(bipy)} with MeI to produce the monoorganohalopalladium(II) complex {PdRI(bipy)}, containing the methyl substituted biphenyl ligand, equation 5.6-1. The formation of a palladium(IV) intermediate was proposed, and although a structure was not suggested it is interesting to note that an identical reaction with the platinum analogue {Pt(biph)(bipy)} gave *cis* addition of MeI, equation 5.6-2.



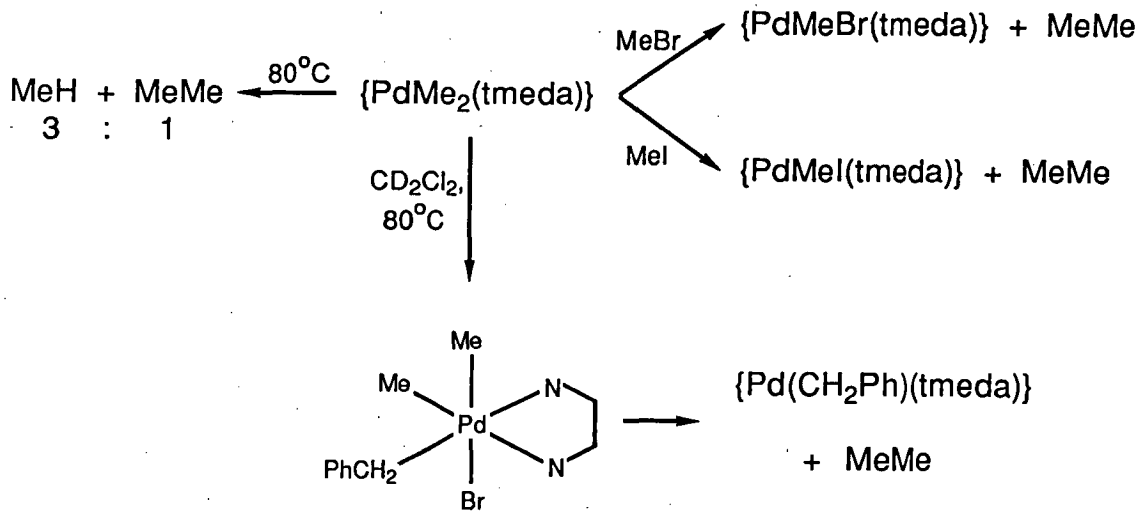
5.6-1



5.6-2

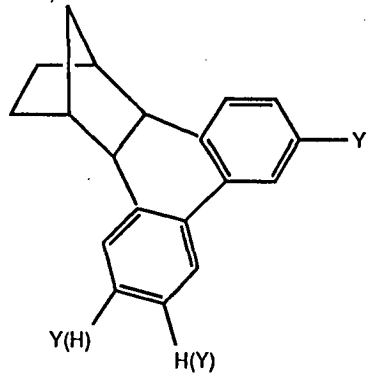
The thermolysis of {$PdMe_2$(tmeda)} in benzene at 80°C has been reported to yield a 3:1 mixture of methane and ethane,[88] scheme 5.6-1. However, reaction of {$PdMe_2$(tmeda)} with the electrophiles MeI, MeBr, and $PhCH_2Br$ readily gave the complexes {PdMeI(tmeda)}, {PdMeBr(tmeda)} and {$Pd(CH_2Ph)Br$(tmeda)} respectively, together with one equivalent of ethane, compelling evidence for palladium(IV) intermediacy. Indeed, an *in situ* reaction between {$PdMe_2$(tmeda)} and $PhCH_2Br$ in CD_2Cl_2 at -30°C resulted in detection of a palladium(IV) complex exhibiting *cis* addition of $PhCH_2Br$, scheme 5.6-1.

Scheme 5.6-1.

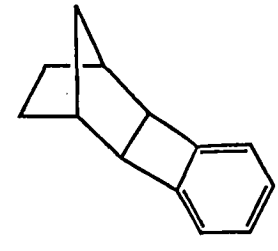


The participation of palladium(IV) intermediates has been proposed for the palladium catalysed reaction of bromobenzenes with [2.2.1]hept-2-ene,[90] leading to the formation of products such as those portrayed in Figure 5.6-1.

Figure 5.6-1.



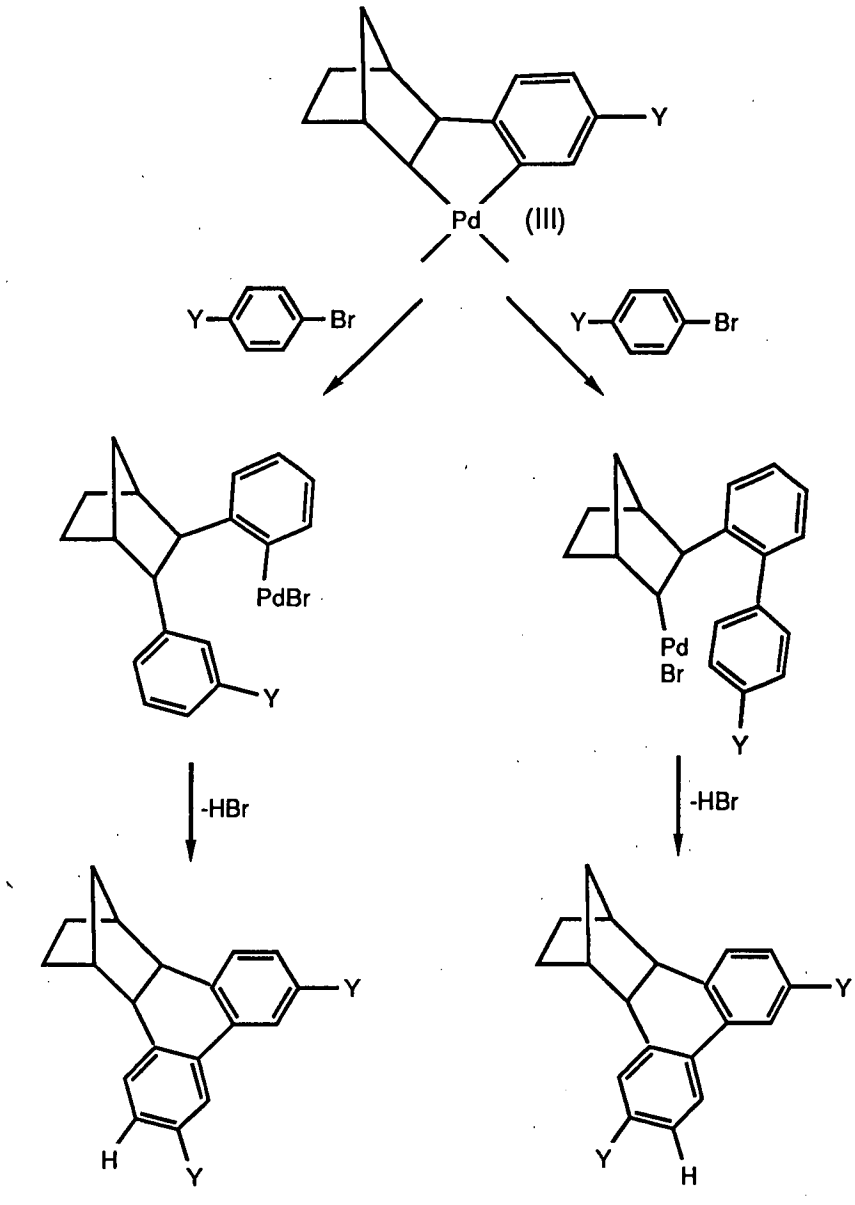
(I)



(II)

Scheme 5.5-2 depicts the mechanism proposed for the formation of I, and involves interaction of bromobenzene with the metallacycle III. Further, the possible involvement of a palladium(IV) intermediate was suggested.[90b]

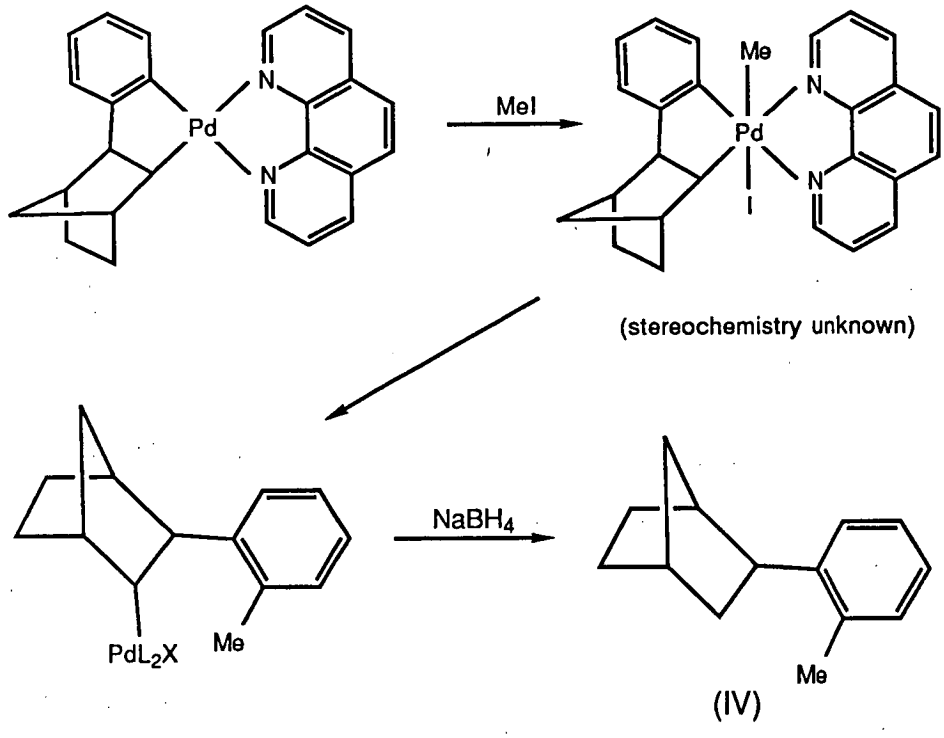
Scheme 5.5-2.



Support for this proposal was obtained upon reaction of a similar metallacycle, containing the N-donor ligand phenanthroline, in order to stabilise the palladium(IV) intermediate, with MeI scheme 5.6-3. An *in situ* reaction in $CDCl_3$ at -20°C gave a spectrum displaying the presence of a palladium(IV) complex with Pd^{IV}-Me at 2.13 ppm, although the stereochemistry of this complex was not elucidated.[89] Warming

resulted in reductive coupling of the methyl and phenyl groups, and upon addition of $NaBH_4$ the organic compound IV was produced.[89] The complexes depicted in scheme 5.6-3 were proposed to be stabilised versions of the species involved in catalytic processes previously described by Chiusoli and co-workers.

Scheme 5.5-3.



5.7 STRUCTURE AND STABILITY OF PALLADIUM(IV) COMPLEXES

Alkylpalladium(IV) chemistry is in its infancy, and is represented almost entirely by the work presented in this thesis. This section seeks to draw together some of the more general observations on palladium(IV) chemistry, and to account for trends in stability and reactivity. Only a selection of topics are discussed, with emphasis on those that provide a guide to future synthetic and mechanistic studies, and much of the discussion is speculative.

An important factor which contributes to the stability of organopalladium(IV) complexes, and indeed inorganic palladium(IV) complexes also, is the nature of the ancillary ligands present. The inability of phosphorus based ligands to stabilise the +4 oxidation state is demonstrated by the paucity of such inorganic complexes, with no organopalladium(IV) complexes containing phosphorous based ligands known. In comparison, it is apparent from previous reports that nitrogen donor ligands stabilise inorganic palladium(IV) complexes, and the results presented here establish this also for alkylpalladium(IV) derivatives.

For bidentate N-donor ligand complexes, both the stability of isolated complexes and *in situ* N.M.R. experiments of the reaction between MeI and the complexes $\{PdMe_2(L_2)\}$ establish an order of decreasing stability of the palladium(IV) complexes as a function of L_2,

bipy,

$mim_2C{=}CH_2$ > methanes (R_2CH_2) ~ ethanes (R_2CHMe) > propanes (R_2CMe_2)

etc.

For example, an *in situ* reaction between MeI and $\{PdMe_2(pymimC{=}O)\}$ produces a stable palladium(IV) complex at 0°C, but in a similar reaction with $\{PdMe_2(pymimCHMe)\}$ a much lower reaction temperature is required (*ca.* -30°C) to prevent reductive elimination from the palladium(IV) complex.

For the flexible bidentates, the nature of the bridging groups (CHMe, CMe_2) is more important than the donor ability of the ligands (mim > py > pz) or any effect of donor ring size (5 membered vs. 6 membered) on the chelate geometry. The low stability of R_2CMe_2 complexes may be readily attributed to excessive Pd^{IV}-Me···CMe or Pd^{IV}-I···CMe interactions or Pd^{IV}-solvent···CMe interactions in cations $[PdMe_3(S)(L_2)]^+$, favouring five coordination and thus reductive elimination since reductive elimination for $\{PdMe_3I(bipy)\}$ clearly involves at least partial ionisation of iodide. Although reductive elimination from $\{PdMe_3I(bipy)\}$ involves at least partial ionisation of iodide, and this process may not be affected by replacement of bipy with

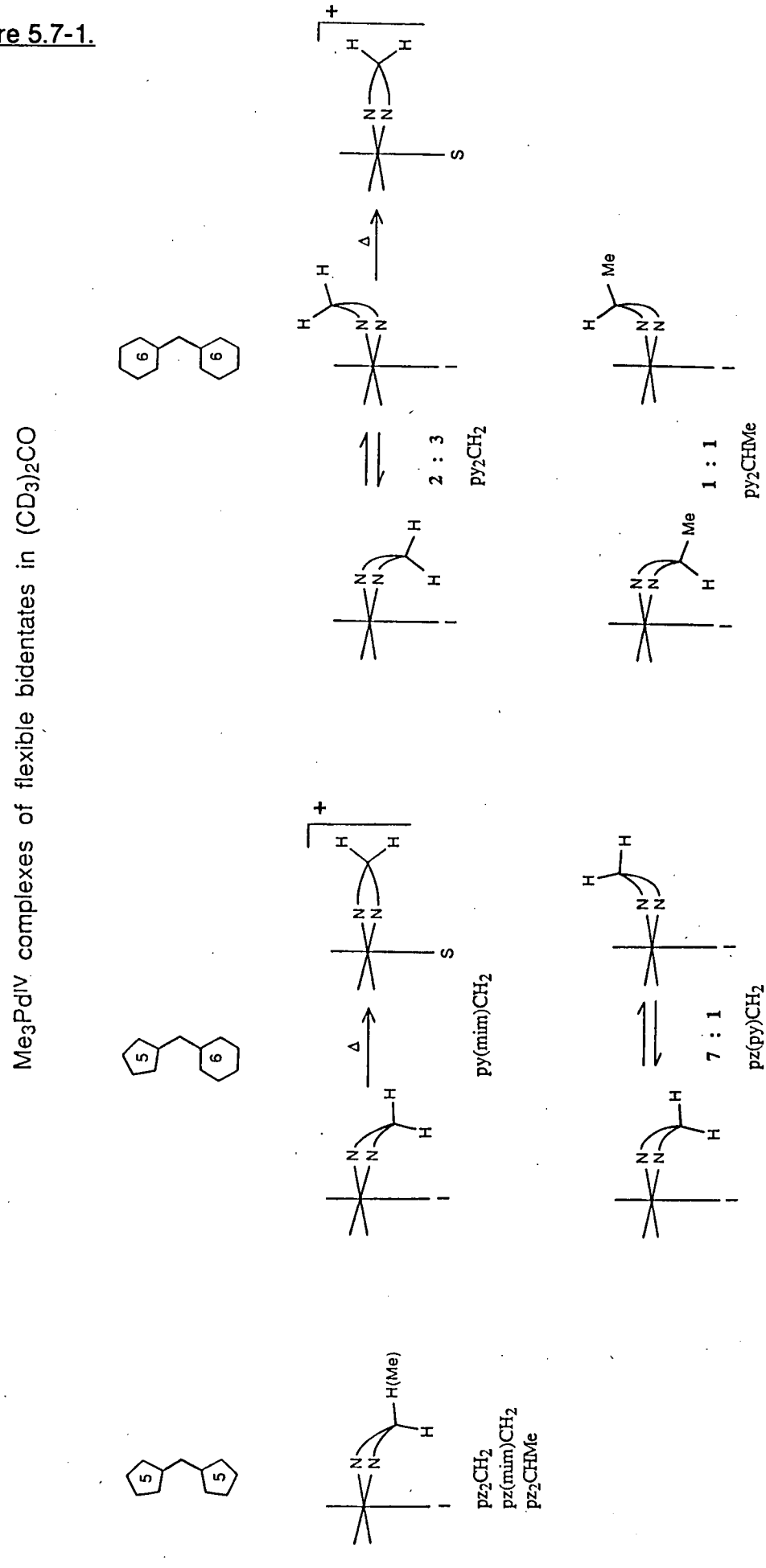
flexible bidentates, the flexible bidentates are expected to facilitate reductive elimination as they are more able to accommodate any geometry changes during reductive elimination more easily than the planar ligands, *e.g.* they can form larger N-Pd-N angles.

The structures adopted by the methane and ethane bridged ligand complexes {$PdMe_3I(R_2CH_2)$} and {$PdMe_3I(R_2CHMe)$} are shown in figure 5.7-1. Figure 5.7-1 does not include complexes of the ligands pymimCHMe and mim_2CHMe, since definitive structural assignment was not possible for their complexes.

It does not appear possible, at this stage of the development of organopalladium(IV) chemistry, to fully explain the range of behaviour summarised in figure 5.7-1. However, it is notable that the palladium(IV) complexes of ethane bridged ligands containing pyridine and/or pyrazole donor groups exhibit a structure with the bridgehead methyl group in an equatorial orientation to avoid close Pd^{IV}-Me···CMe or Pd^{IV}-I···CMe interactions. Palladium(IV) complexes of methane and ethane bridged ligands containing two five membered rings, or a five and a six membered ring, exhibit a strong preference for the bridgehead proton to be in an axial orientation adjacent to the iodo-group, although complexes containing two six membered rings show little or no preference for this orientation. The different behaviour observed between these two systems may be related to the increased puckering of the chelate ring in the latter complexes compared with the former.

The reaction of MeI with ethane bridged ligand complexes (R_2CHMe) can potentially produce two isomers, which are not interconvertible by boat to boat ring inversion. Indeed, the *in situ* reaction between {$PdMe_2(py_2CHMe)$} and MeI at ambient temperature produced two Pd(IV) isomers (which did not interconvert) in *ca.* 1:1 ratio. As the palladium(II) complex {$PdMe_2(py_2CHMe)$} has been observed to exhibit rapid equilibrium between two conformers in *ca.* 1:1 ratio, related by boat to boat ring inversion, the S_N2 mechanism for oxidative addition established for {$PdMe_2(bipy)$} is consistent with this result. Thus, nucleophilic attack of palladium on MeI from the least sterically hindered face of palladium gives the ionic intermediates shown, figure 5.7-2, with the expected *trans* oxidative addition giving the products in

Figure 5.7-1.


Me3PdIV complexes of flexible bidentates in (CD3)2CO
6
6
Δ
2 : 3
py2CH2
1 : 1
py2CHMe
5
6
Δ
py(mim)CH2
7 : 1
pz(py)CH2
5
5
H(Me)
pz2CH2
pz(mim)CH2
pz2CHMe

1:1 ratio. However, {$PdMe_2(pz_2CHMe)$} also adopts two structures, in *ca.* 1:2 ratio, but reaction with MeI produces only one palladium(IV) isomer. This could result from higher reactivity of one {$PdMe_2(pz_2CHMe)$} conformer towards oxidative addition, or it may result from intramolecular scrambling of methyl groups in intermediates to give the preferred isomer, figure 5.7-3. The latter alternative is feasible since scrambling of CH_3 and CD_3 groups on reaction of CD_3I with {$PdMe_2(bipy)$} occurs, and in this case an S_N2 mechanism is well established; for the less labile metal platinum the oxidative addition of CD_3I to {$PtMe_2(bipy)$} occurs in a *trans* fashion with slower scrambling observed by N.M.R. spectroscopy. In this respect, oxidative addition of organohalides to {$PdMe_2(pymim_2CH)$} is of particular interest, since this complex adopts only **one** conformation in solution, with an axial pyridine, and if an S_N2 mechanism is assumed (at least for EtI) only **one** isomer (A) is expected in the absence of scrambling, figure 5.7-4, in contrast with the two isomers observed.

The "leaving group preferences" of {$PdMe_2R'X(bipy)$} ($R'X=CD_3I$, EtI, $CH_2=CHCH_2Br$), and the Pd(IV) complexes formed by {$PdMe_2(pz_2CMe_2)$}, were investigated and the results are listed in table 5.7-1. For both series of complexes studied there was a pronounced preference for elimination of methyl groups to produce ethane. For elimination from {$PdMe_2R'X(bipy)$} the series Me > Et ~ CD_3 > $CH_2=CHCH_2$ > $PhCH_2$ represents the decreasing ease of elimination of alkyl groups, and it is interesting to compare this series with that found for platinum(IV), MeCO > $CH_2=CHCH_2$ ~ Et > Me > CD_3 > $PhCH_2$ > Ph > CF_3.[71]

Prediction of expected reductive elimination products is not straightforward, except for {$PdMe_2(CD_3)I(bipy)$} where the Me and CD_3 groups are known to be scrambled prior to reductive elimination. Thus, assuming a five coordinate intermediate, with or without preference for elimination of groups *trans* to bipy or the vacant site, then the ratio MeMe:2MeCD_3 is expected. However, for {$PdMe_2R'X(bipy)$} ($R'X=PhCH_2Br$), where R' is *trans* to the bromo-group, then in the absence of scrambling, only MeR' is expected if concerted reductive elimination of two groups *trans* to bipy is precluded (orbital symmetry arguments, section 5.4). It is

Figure 5.7-2.

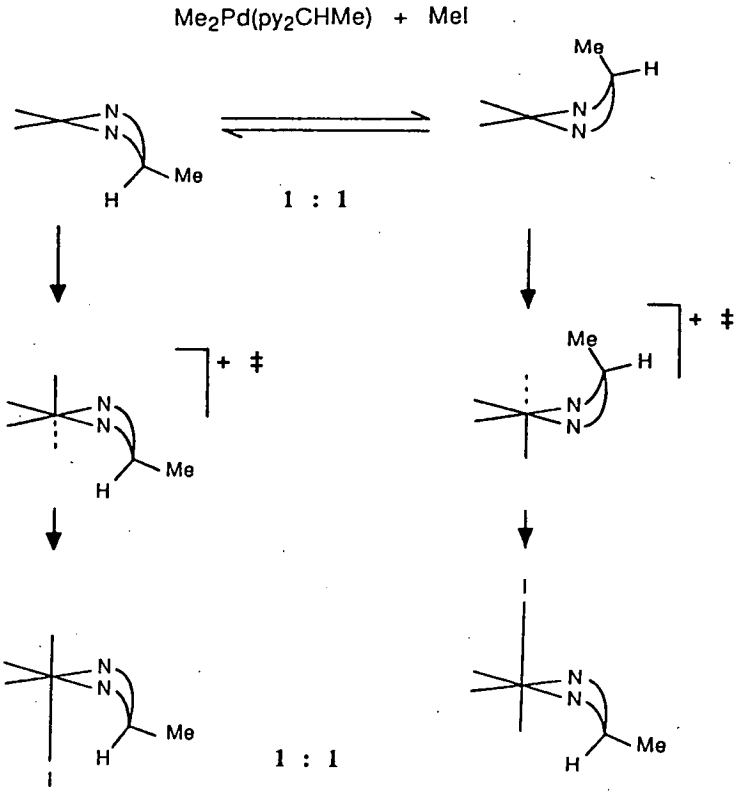


Figure 5.7-3.

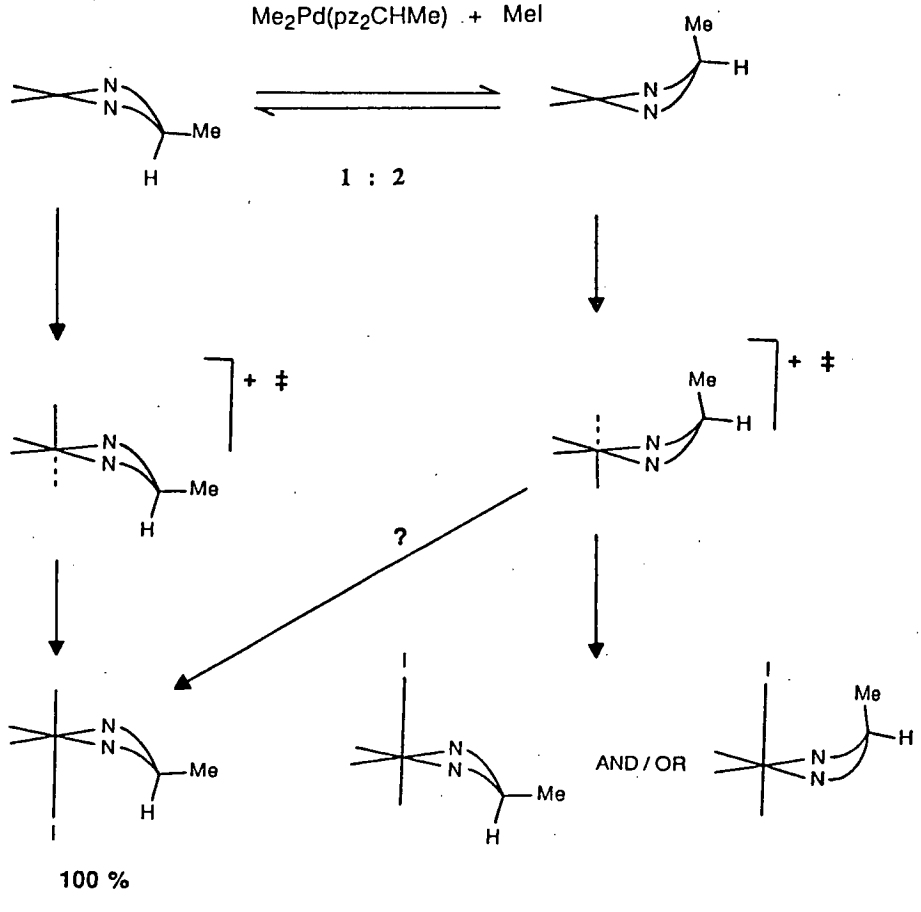


Figure 5.7-4.

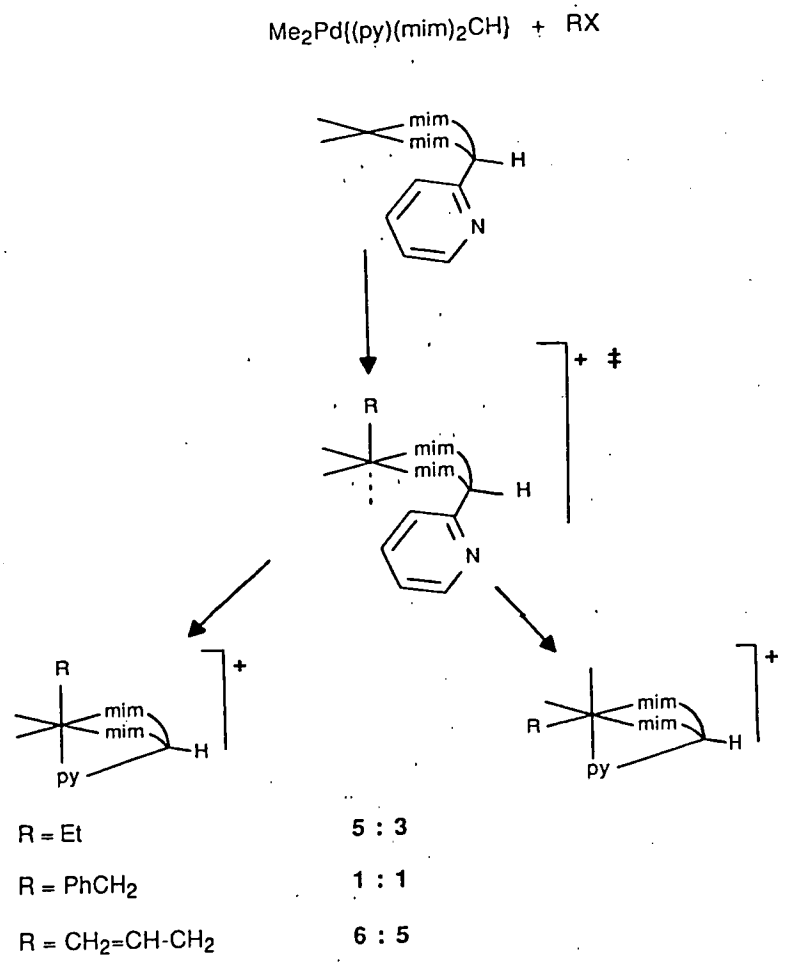


Table 5.7-1 Proportions of MeMe and MeR' from Reductive Elimination

	{$PdMe_2R'X(bipy)$}		"$Pd^{IV}Me_2R'X(pz_2CMe_2)$"*	
R'X	MeMe	MeR'	MeMe	MeR'
CD_3I	1	1	1	1
EtI	1	1	1	1
$CH_2=CHCH_2Br$	5	1	10	1
$PhCH_2Br$	9	1	1	1

*Structure of Pd^{IV} species not known.

assumed that scrambling does occur for the five coordinate intermediate, allowing reductive elimination to occur for the better leaving group.

Palladium(IV) complexes containing tridentate ligands have been studied less exhaustively than their bidentate analogues, but two factors affecting the stability of these complexes are apparent. Firstly, complexes containing weak donor ligands are more susceptible towards reductive elimination than stronger donor ligand complexes, and secondly, replacement of the iodide anion by a "non-coordinating" anion produces more stable palladium(IV) cations. For example, $[PdMe_3(pymim_2CH)]I$ is stable in acetone-D6 even upon heating to *ca.* 60°C, but $[PdMe_3(pz_2RCH)]I$ (R=pz, py, mim) undergo reductive elimination of ethane at ambient temperature, although $[PdMe_3(pz_3CH)]BF_4$ is stable at ambient temperature. The coordination of iodide is a key step in the reductive elimination mechanism, and results in the attainment of greater flexibility for the ligand, allowing elimination to proceed as for $\{PdMe_3I(bipy)\}$ without opening of the remaining NMN angle.

To summarise, oxidative addition of a selection of simple alkyl halides to $Pd^{II}Me_2$ complexes of N-donor ligands occurs readily to form palladium(IV) complexes which may be detected spectroscopically or isolated, or reductively eliminate organic groups to give monoalkylpalladium(II) products. The formation of five coordinate cationic intermediates has been demonstrated to play a major role in palladium(IV) chemistry, with oxidative addition, reductive elimination and intramolecular scrambling of alkyl groups occurring from such intermediates. Moreover, the feasibility of a palladium(II)-palladium(IV) cross coupling mechanism has been demonstrated, and although palladium(IV) intermediates containing N-donor ligands are yet to be attained in catalytic cycles, they do at least represent stabilised models for proposed palladium(IV) phosphine intermediates.

REFERENCES

1. Gulliver, D.J. and Levason, W.,
   Coord. Chem. Rev., **46** (1982) 1.
2. Gulliver, D.J., and Levason, W.,
   J. Chem. Soc. Dalton Trans., (1982) 1895.

3.(a) Gray, L.R., Gulliver, D.J., Levason, W., and Webster, M.
   J. Chem. Soc. Dalton Trans., (1983) 133.

3.(b) Clark, R.J.H., Croud, V.B., and Kurmoo, M.,
   J. Chem. Soc. Dalton Trans., (1985) 815.

4. Toriumi, K., Yamashita, M., Ito, H., Ito, T.,
   Acta Cryst., **C42** (1986) 963.

5.(a) Livingstone, S.E.,
   "The Chemistry of Ruthenium, Rhodium, Palladium, Osmium, Iridium and Platinum", Pergamon Press, Oxford, 1973.
   Barnard, C.F.J., and Russell, M.J.H.,
   "Palladium" in "Comprehensive Coordination Chemistry"
   Wilkinson, G., Gillard, R.D., and McCleverty, J.A. (Eds.),
   Pergamon Press, Oxford, 5 (1987) 1099.

(b) Hartley, F.R.,
   "The Chemistry of Platinum and Palladium",
   Applied Science Publishers Ltd., London, 1973.

6. Maitlis, P.M., Espinet, P., and Russell, M.J.H.,
   "Compounds with Palladium-Carbon σ-Bonds" in "Comprehensive Organometallic Chemistry", Wilkinson, G., Stone, F.G.A., and Abel, E.W. (Eds.), Pergamon Press, Oxford, 6 (1982) 279.
7. Uson, R., Fornies, J., and Navarro, R.
   J. Organomet. Chem., **96** (1975) 307.
8. Uson, R., Fornies, J., and Navarro, R.,
   Syn. React. Inorg. Metal-Org. Chem., 7 (1977) 235.

9. Roe, D.M., Calvo, C., Krishnamachari, N., and Maitlis, P.M.,
J. Chem. Soc. Dalton Trans., (1975) 125.

10. Nyholm, R.S., and Royo, P.,
J. Chem. Soc. Chem. Commun., (1969) 421.

11. Royo, P.,
Rev. Acad. Ciencias, Zaragoza, **27** (1972) 235.

12. Nyholm, R.,
Quart. Rev., **24** (1970)1.

13. Uson, R., Royo, P., Fornies, J., and Martinez, F.,
J. Organomet. Chem., **90** (1975) 367.

14. Zakharkin, L.I., and Kovredov, A.I.,
J. Gen. Chem. (U.S.S.R.), **44** (1974) 1796.

15. Ketley, A.D., Fisher, L.P., Berlin, A.J., Morgan, C.R., Gorman, E.H. and Steadman, T.R.,
Inorg. Chem., **6** (1967) 657.

16. Backvall, J.,
Tetrahedron Lett., **26**(1975) 2225.

17. Maitlis, P.M.,
"The Organic Chemistry of Palladium", Academic Press, 1971, Vol. 1.

18. Ito, T., Tsuchiya, H., and Yamamoto, A.,
Bull. Chem. Soc. Jpn., **50** (1977), 1319.
Ozawa, F., Kurihara, K., Yamamoto, T., and Yamamoto, A.,
Bull. Chem. Soc. Jpn., **58** (1985) 399.

19. Henry, P.M.,
Adv. Organomet. Chem., **13** (1975) 363.

20.(a)Stille, J.K., and Lau, K.S.Y.,
J. Am. Chem. Soc., **98** (1976) 5841.

(b)Milstein, D., and Stille, J.K.,
ibid, **101** (1979) 4981, 4992.

(c) Gillie, A., and Stille, J.K.,

ibid., **102** (1980) 4933.

(d) Loar, M.K., and Stille, J.K.,

ibid, **103** (1981) 4174.

(e) Moravskiy, A., and Stille, J.K.,

ibid, **103** (1981) 4182.

21. Weinberg, E.L., Hunter, B.K., and Baird, M.C.,

J. Organomet. Chem., **240**.(1982) 95.

22. Roundhill, D.M.,

"Platinum" in "Comprehensive Coordination Chemistry",

Wilkinson, G., Gillard, R.D., and McCleverty, J.A. (Eds).

Pergamon Press, Oxford, 5 (1987) 351.

Hartley, F.R.,

"Platinum" in "Comprehensive Organometallic Chemistry",

Wilkinson, G., Stone, F.G.A., and Abel, E.W. (Eds.),

Pergamon Press, Oxford, 6 (1982) 471.

23. Jain, V.K., Rao, G.S., and Jain, L.,

Adv. Organomet. Chem., 27 (1987) 113.

24. Nicolaou, K.C., and Webber, S.E.,

Synthesis, (1986) 453.

25. Yamada, J., and Yamamoto, Y.,

J. Chem. Soc. Chem. Commun., (1987) 1302.

26. Miyaura, N., Satoh, M., and Suzuki, A.,

Tetrahedron Lett., **27** (1986) 3745.

27. Hayashi, T., Konishi, M., Yokota, K., and Kumada, M.,

J. Chem. Soc. Chem. Commun., (1981) 313.

28. Negishi, E., and Luo, F.,

J. Org. Chem., **48** (1983) 1560.

29. Echavarren, A.M., and Stille, J.K.,

J. Am. Chem. Soc., **110** (1988) 1557.--

30. Stille, J.K., and Simpson, J.H.,

J. *Am. Chem. Soc.*, **109** (1987) 2138.

31. Dang, H.P., and Linstrumelle, G.,

Tetrahedron Lett., (1978) 191.

32. Wakita, Y., Yasunaga, T., and Kojima, M.,

J. Organomet. Chem., **288** (1985) 261.

33. Hayashi, T., Konishi, M., Kobori, Y., Kumada, M., Higuchi, T., and Hiritsu, K.,

J. Am. Chem. Soc., **106** (1984) 158.

34. Yamamoto, Y., Hatsuya, S., and Yamada, J.,

J. Chem. Soc. Chem. Commun., (1988) 86.

35. Sheffy, F.K., Godschalx, J.P., and Stille, J.K.,

J. Am. Chem. Soc., **106** (1984) 4833.

36. Sekiya, A., and Ishikawa, N.,

J. Organomet. Chem., **118** (1976) 349.

37. Bumagin, N.A., Kalinovskii, I.O., and Beletskaya, I.P.

J. Organomet. Chem., **267** (1984) C1.

38. Stille, J.K., and Groh, B.L.,

J. Am. Chem. Soc., **109** (1987) 813.

39. Echavarren, A.M., and Stille, J. K.,

J. Am. Chem. Soc., **109** (1987) 5478.

40. Sustmann, R., Lau, J., and Zipp, M.,

Tetrahedron Lett., **27** (1986) 5207.

41. Beletskaya, I.P.,

J. Organomet. Chem., **250** (1983) 551.

42. Negishi, E.,

Acc. Chem. Res., **15** (1982) 340.

43. Maitlis, P.M., Espinet, P., and Russell, M.J.H.,
"Complexes of Palladium(0)" in "Comprehensive Organometallic Chemistry", Wilkinson, G., Stone, F.G.A., and Abel, E.W. (Eds.), Pergamon Press, Oxford, 6 (1982) 243.

44. Negishi, E., Takahashi, T., and Akiyoshi, K.,
J. Chem. Soc. Chem. Commun., (1986) 1338.

45. Hayashi, T., Konishi, M., Okamoto, Y., Kabeta, K., Kumada, M.,
J. Org. Chem., 51 (1986) 3772.

46. Minato, A., Suzuki, K., and Tamao, K.,
J. Am. Chem. Soc., 109 (1987) 1257.

47. Hayasi, Y., Riediker, M., Temple, J.S., and Schwartz, J.,
Tetrahedron Lett., (1981) 2629.

48. Negishi, E., Takahashi, T., Baba, S., Van Horn, D.E., and Okukado, N.,
J. Am. Chem. Soc., 109 (1987) 2393.

49. Stille, J.K.,
Pure and Appl. Chem., 57 (1985) 1771.

50. Stille, J.K.,
Angew. Chem. Int. Engl. Ed., 25 (1986) 508.

51. Negishi, E., Valente, L.F., and Kobayashi, M.,
J. Am. Chem. Soc., 102 (1980) 3298.
Kobayashi, M., and Negishi, E.,
J. Org. Chem., 45 (1980) 5223.
Simpson, J.H., and Stille, J.K.,
J. Org. Chem., 50 (1985) 1759.

52. The reader is referred to the following reviews and monographs which formed the basis of the following discussion.
Stille, J.K., and Lau, K.S.Y.,
Acc. Chem. Res., 10 (1977) 434.
Collman, J.P.,

Acc. Chem. Res., **1** (1968) 136.

Collman, J.P., Hegedus, L.S., Norton, J.R., and Finke, R.G.,
"Principles and Applications of Organotransition Metal Chemistry",
University Science Books, California, 1987.

Kochi, J.K.,
"Organometallic Mechanisms and Catalysis", Academic Press,
London, 1978.

Stille, J.K.,
"Oxidative Addition and Reductive Elimination", in
"The Chemistry of the Metal-Carbon Bond", Hartley, F.R.,
and Patai, S. (Eds.), John Wiley and Sons, Chichester, 1985.

Braterman, P.S., and Cross, R.J.,
Chem. Soc. Rev., **2** (1973) 271.

Baird, M.C.,
J. Organomet. Chem., **64** (1974) 289.

Davidson, P.J., Lappert, M.F., and Pearce, R.,
Chem. Rev., **76** (1976) 219.

Halpern, J.,
Acc. Chem. Res., **15** (1982) 332.

Yamamoto, A., Yamamoto, T., Komiya, S., and Ozawa, F.,
Pure Appl. Chem., **56** (1984) 1621.

Ozawa, F., Ito, T., Nakamura, Y., and Yamamoto, A.,
Bull. Chem. Soc. Jpn., **54** (1981) 1868.

Tatsumi, K., Nakamura, A., Komiya, S., Yamamoto, A., and
Yamamoto, T.,
J. Am. Chem. Soc., **106** (1984) 8181

53. Milstein, D.,
Acc. Chem. Res., **17** (1984) 221.

Atwood, J.D.,
Coord. Chem. Rev., **83** (1988) 93.

54. Morrison, R.T., and Boyd, R.N.,
"Organic Chemistry", Allyn and Bacon, Inc., London, 1980.

55. Terheijden, J., van Koten, G., Vinke, I.C., and Spek, A.L.,
J. Am. Chem. Soc., **107** (1985) 2891.

56(a)Puddephatt, R.J., and Scott, J.D.,
Organometallics, **4** (1985) 1221.

(b)Crespo, M., and Puddephatt, R.J.
Organometallics, in press, 1988.

57. Kochi, J.K.
Acc. Chem. Res., 7 (1974) 351.
Lappert, M.F., and Lednor, P.W.,
Adv. Organomet. Chem., **14** (1976) 345.
Chanon, M.,
Bull. Soc. Chim. Fr., (1982) II-97.
Eisch, J.J.,
Pure Appl. Chem., **56** (1984) 35.

58. See, for example,
Maitlis, P.M.,
"The organic chemistry of Palladium", vol. 2, Academic Press,
London, 1971.
Tsuji, J.
"Organic Synthesis with Palladium Compounds", Springer-Verlag,
Berlin, 1980.

59. Kramer, A.V., and Osborn, J.A.,
J. Am. Chem. Soc., **96** (1974) 7832.

60. Lau, K.S.Y., Wong, P.K., and Stille, J.K.,
J. Am. Chem. Soc., **98** (1976) 5832.
Becker, Y., and Stille, J.K.,
J. Am. Chem. Soc., **100** (1978) 838.

61. Smith, G., and Kochi, J.K.,
J. Organomet. Chem., 198 (1980) 199.

62. Appleton, T.G., Clark, H.C., and Manzer, L.E.,
J. Organomet. Chem., **65** (1974) 275.

63. Tatsumi, K., Hoffmann, R., Yamamoto, A., and Stille, J.K.,
Bull. Chem. Soc. Jpn., **54** (1981) 1857.

64. Cross, R.J.,
In "The Chemistry of the Metal-Carbon Bond", Hartley, F.R.,
and Patai, S. (Eds.), John Wiley and Sons, Chichester, 1985.

65. See, for example,
Sustmann, R., and Lau, J.,
Chem. Ber., **119** (1986) 2531.
Diversi, P., Ingrosso, G., Lucherini, A., Lumini, T., Marchetti, F.,
Adovasio, V., and Nardelli, M.,
J. Chem. Soc. Dalton Trans., (1988) 133.

66. Gretz, E., and Sen, A.,
J. Am. Chem. Soc., **108** (1986) 6038.
Van Leeuwen, P.W.N.M., Roobeek, C.F., and Huis, R.,
J. Organomet. Chem., **142** (1977) 233.

67. Parshall, G.W.,
J. Am. Chem. Soc., **96** (1974) 2360.

68. Kurosawa, H., Emoto, M., and Urabe, A.,
J. Chem. Soc. Chem. Commun., (1984) 968.

69(a)Ozawa, F., Fujimori, M., Yamamoto, T., and Yamamoto, A.,
Organometallics, 5 (1986) 2144.

(b) Ozawa, F., Hidaka, T., Yamamoto, T., and Yamamoto, A.,
J. Organomet. Chem., **330** (1987) 253.

70. Monaghan, P.K., and Puddephatt, R.J.,
J. Chem. Soc. Dalton Trans., (1988) 595.

71. Brown, M.P., Puddephatt, R.J., and Upton, C.E.E.,
J. Chem. Soc. Dalton Trans., (1974) 2457.

72. Ettorre, R.,
Inorg. Nucl. Chem. Lett., 5 (1969) 45.

73. Clark, H.C., Ferguson, G., Jain, V.K., and Parvez, M.,
J. Organomet. Chem., **270** (1984) 365.

74. Byers, P.K., Canty, A.J., Crespo, M., Puddephatt, R.J., and Scott, J.D.
Organometallics, 7 (1988) 1363.

75. Brookhart, M., and Green, M.L.H.,
J. Organomet. Chem., **250** (1983) 395.

76. Pauling, L.,
"The Nature of the Chemical Bond", Cornell University Press, Ithaca, 1960.

77. Bondi, A.,
J. Phys. Chem., **68** (1964) 441.

78. Burk, M.J., Segmuller, B., and Crabtree, R.H.,
Organometallics, 6 (1987) 2241.

79. King, R.B., and Bond, A.,
J. Am. Chem. Soc., **96** (1974) 1338.

80. Wisner, J.M., Bartczak, T.J., and Ibers, J.A.,
J. Am. Chem. Soc., **108** (1986) 347.
Wisner, J.M., Bartczak, T.J., and Ibers, J.A.,
Organometallics, 5 (1986) 2044.

81. Braterman, P.S.,
J. Chem. Soc. Chem. Commun., (1979) 70.
Braterman, P.S.,
Topics in Current Chemistry, **92** (1980) 149.

82. Paiaro, G., and Musco, A.,
Tetrahedron Lett., (1965) 1583.

83. Goodfellow, R.J., and Venanzi, L.M.,
J. Chem. Soc. (A), (1966) 784.

84. Hegedus, L.S., Åkermark, B., Olsen, D.J., Anderson, O.P., and Zetterberg, K.,
J. Am. Chem. Soc., **104** (1982) 697.

85. Byers, P.K., Canty, A.J., Skelton, B.W., and White, A.H.
J. Chem. Soc. Chem. Commun., (1986) 1722; (1987) 1093.
Byers, P.K., Canty, A.J., Skelton, B.W., and White, A.H.
J. Organomet. Chem. **336** (1987) C55.

86. Kurosawa, H., Emoto, M., and Kawasaki, Y.,
J. Organomet. Chem., **346** (1988) 137.

87. Cornioley-Deuschel, C., and von Zelewsky, A.
Inorg. Chem., **26** (1987) 3354.

88. de Graaf, W., Boersma, J., Grove, D., Spek, A.L., and van Koten, G.
Rec. Trav. Chim. Pays-Bas, **107** (1988) 299.

89. Catellani, M., and Chiusoli, G.P.
J. Organomet. Chem., **346** (1988) C27.

90(a) Bocelli, G., Catellani, M., and Chiusoli, G.P.
J. Organomet. Chem., **279** (1984) 225.

(b) Catellani, M., and Chiusoli, G.P.,
Ibid., **286** (1985) C13.

(c) Catellani, M., Chiusoli, G.P., and Ricotti, S.
Ibid. **296** (1985) C11.

CHAPTER 6

EXPERIMENTAL

6.1 GENERAL INTRODUCTION AND PURIFICATION OF REAGENTS

Infrared Spectra were recorded on a Hitachi 270-30 Infrared Spectrophotometer as neat liquids or as nujol mulls between NaCl plates. Far infrared spectra were recorded with a Perkin-Elmer 577 spectrophotometer (600-200 cm^{-1}) as nujol mulls between polyethylene plates, or on a Digilab FTS-20E Fourier Transform Infrared spectrophotometer (500-100 cm^{-1}) as polyethylene disks. Absorptions are described as strong (s), medium (m), or weak (w) in intensity.

^{1}H.N.M.R. Spectra were recorded using a Bruker AM 300 Spectrometer. Chemical Shifts (δ) are given in parts per million (ppm) relative to tetramethylsilane (TMS) in deuterated chloroform, acetone, or acetonitrile, as indicated. Resonances are described as singlets (s), doublets (d), triplets (t), quartets (q), multiplets (m), or combinations thereof.

Mass Spectra were obtained using a Vacuum General Micromass 7070F Spectrometer and are reported in descending m/e ratio.

Microanalyses were performed by the Australian Microanalytical Service, Melbourne or the Canadian Microanalytical Service, Vancouver on samples dried at room temperature *in vacuo*. Melting points were determined with a Reichart Thermo apparatus and stereomicroscope, and are reported uncorrected.

Molecular Weights were determined using a Knauer vapour phase osmometer in chloroform at either 25°C or 37°C (as indicated) for $1\text{-}3\times10^{-2}$M solutions.

Conductivities were measured at 25°C using 10^{-3}M acetone solutions with a Philips PW9504/00 conductivity meter and a Griffin and George conductivity cell; the cell constant was determined using standard KCl solutions.

General purpose solvents and reagents were used as received. Solvents for recrystallisation were distilled after preliminary drying according to Perrin, Armarego, and Perrin.[1] Purification methods for commonly used solvents and reagents are listed

below; methods used are similar to those recommended by Perrin, Armarego, and Perrin.

Acetone: Addition of $KMnO_4$ at acetone reflux until the violet colour persists, followed by drying over $CaSO_4$ and distillation.

Allylbromide: Dried over $CaCl_2$, followed by fractional distillation in the dark and storage in the dark.

Benzene: Washed with concentrated H_2SO_4, water, 2M NaOH, then refluxed and distilled from P_2O_5 and stored over sodium wire.

Benzylbromide: Dried over $CaCl_2$, followed by fractional distillation under reduced pressure (*ca.* 20 mmHg) in the dark and storage in the dark.

Bromobenzene: Predried over $CaCl_2$, refluxed and distilled from Ca turnings, and stored over 4Å molecular sieves.

2-Bromopyridine: Predried over NaOH, distilled from CaO and stored over 4Å molecular sieves.

Chloroform: Washed with water, predried over $CaCl_2$, then refluxed and distilled from P_2O_5 and stored in the dark.

Diethyl ether: Predried over $CaCl_2$ (24 hours), followed by passage through a column of 4Å molecular sieves, refluxed and distilled from sodium/benzophenone and stored over sodium wire.

Hexane: Refluxed and distilled from sodium/benzophenone and stored over sodium wire.

Iodoethane: Distilled in the dark and stored at -20°C over 4Å molecular sieves.

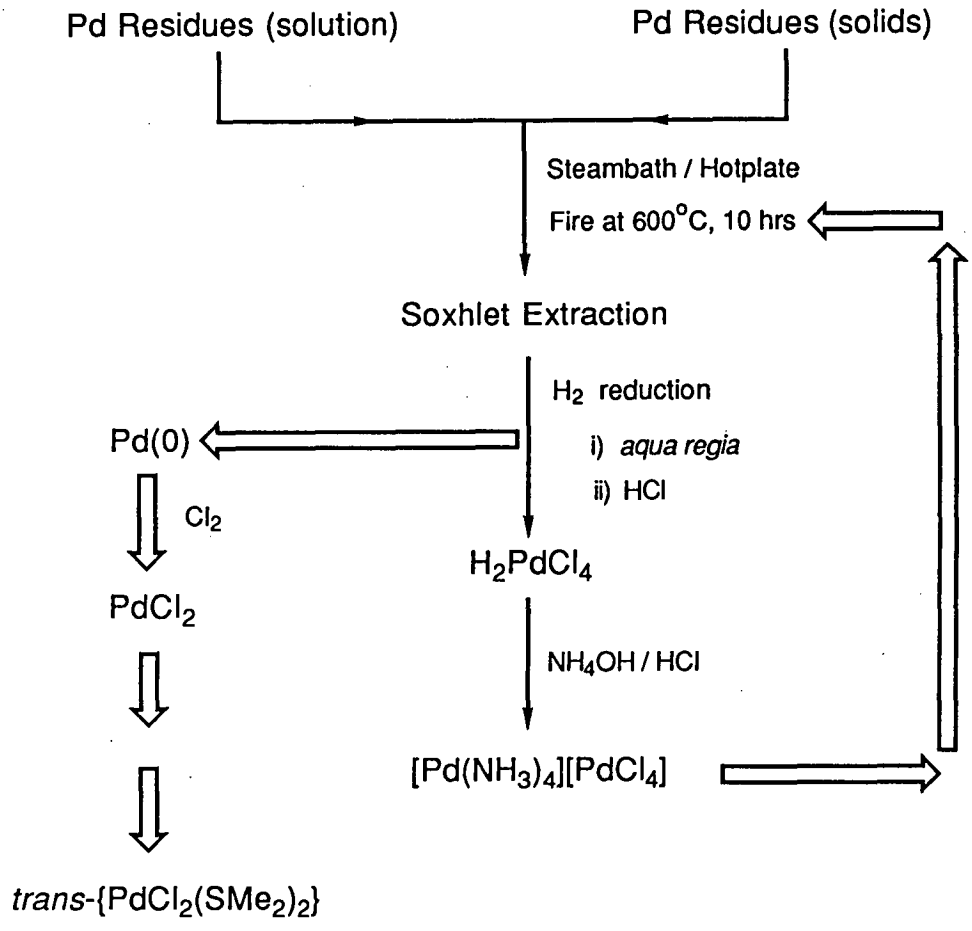
Iodomethane: Distilled and stored at -20°C over 4Å molecular sieves.

Pyridazine:[2] Distilled and stored at -20°C.

Tetrahydrofuran: Predried over KOH, followed by reflux and distillation from sodium/benzophenone and stored over sodium wire.

Palladium Recovery

Recovery Scheme



Solid palladium residues and solutions containing palladium residues were evaporated to a minimum volume on a steam bath. The semi-solid residues were then transferred to a porcelain crucible and heated slowly on a sandbath over a hot plate until virtually all liquids had been evaporated. The residues were then fired in a furnace for 10-12 hours at *ca.* 600°C. On completion the crucible was cooled slowly and the contents soxhlet extracted with water for two hours.

The palladium residues, now free of salts, were placed in a glass tube and flushed with N_2 followed by H_2. While under a H_2 atmosphere the palladium residues were heated with a Bunsen burner until reaction commenced. Reduction of palladium was accompanied by water evolution and scintillation of the metal as the oxide coating was consumed. The reduced palladium was heated and cooled under N_2 to expel absorbed hydrogen.

The metal was then transferred to an evaporating dish and cautiously dissolved in *aqua regia*. When the metal had dissolved the solution volume was lowered over a steam bath and concentrated HCl was added until the evolution of brown fumes had ceased. The resulting deep red solution was then filtered, and treated with concentrated aqueous ammonia to precipitate pink $[Pd(NH_3)_4][PdCl_4]$. This solid was returned through the firing and reduction sequence outlined above to give pure palladium sponge.

6.2 PREPARATION OF INORGANIC PALLADIUM(II) PRECURSORS, ORGANOLITHIUM AND POTASSIUM REAGENTS.

6.2.1 Preparation of Inorganic Palladium(II) Precursors

Palladous Chloride, $PdCl_2$

Palladium metal, from the recovery process, was gently heated under a chlorine atmosphere until reaction had begun. The finely divided metal reacts with evolution of heat to produce red-brown $PdCl_2$ in near quantitative yield.

trans-Bis(benzonitrile)palladium(II) chloride, *trans*-$\{PdCl_2(PhCN)_2\}$.[3]

Palladous chloride was suspended in a large excess of benzonitrile and heated with stirring to *ca.* 100°C. After the majority of $PdCl_2$ had dissolved the solution was rapidly filtered and upon addition of petroleum ether (60-80) yellow $\{PdCl_2(PhCN)_2\}$ precipitated. The solid was isolated by filtration, washed with petrol and air dried.

The filtrate was evaporated of petroleum ether and the remaining benzonitrile saved for future preparations.

***trans*-Bis(dimethylsulphide)palladium(II) chloride, *trans*-{$PdCl_2(SMe_2)_2$}.**

To a solution of *trans*-{$PdCl_2(PhCN)_2$} in benzene was added, with stirring, an excess of dimethylsulphide. Reaction occurred immediately to give a deep red solution which upon evaporation of benzene gave crude *trans*-{$PdCl_2(SMe_2)_2$} as a highly crystalline red solid. Dissolution of this solid in a minimum of hot benzene, followed by rapid filtration and addition of petroleum ether (60-80) afforded *trans*-{$PdCl_2(SMe_2)_2$} as an orange microcrystalline solid. The solid was isolated by filtration, washed with hexane, dried under high vacuum, and stored in a desiccator until required.

Far Infrared : 359(s), 307(m), 288(m), 218(w) cm^{-1}

Literature[4] : 359(s), 308(m), 292(m), 218(mw) cm^{-1}.

***trans*-Bis(dimethylsulphide)palladium(II) bromide, *trans*-{$PdBr_2(SMe_2)_2$}.**

To an acetone solution of *trans*-{$PdCl_2(SMe_2)_2$} was added an excess of KBr in water, and the resulting solution allowed to stir for *ca.* 30 minutes at room temperature. Evaporation of acetone under vacuum gave an orange solid which was isolated by filtration and air dried. Recrystallisation was effected from benzene/petroleum ether as above.

Far Infrared : 316(s), 302(sh), 264(s), 211 (mw) cm^{-1}.

Literature[4] : 315(ms), 302(sh), 262(ms), 210(mw) cm^{-1}.

6.2.2 Preparation of Organolithium and Potassium Reagents

The preparative procedures described in the following pages commonly require the use of methyllithium, *n*-butyllithium, phenyllithium, 2-pyridyllithium, or potassium pyrazolide. In later sections reference to these reagents is brief, *e.g.* "phenyllithium (Li:1.6gm, bromobenzene: 12.2cm^3)" indicates the preparation of

phenyllithium using 1.6gm of lithium and 12.2mls of bromobenzene according to the method outlined below.

Solutions of phenyllithium, 2-pyridyllithium and potassium pyrazolide are generally prepared as required in near quantitative yield, and are subsequently used without titration. In contrast to this, methyllithium and *n*-butyllithium are prepared in somewhat variable yields and both may be stored for later use. As a result, these reagents need to be titrated frequently to estimate the concentration of the lithium reagent present in solution; 1,3-diphenyltosylhydrazone (in tetrahydrofuran at 0°C) has been found to be an effective reagent.[5]

The transfer of these reagents by use of gas tight syringes for small volumes (0.1-20cm^3), or polyethylene tubing for larger volumes, has been found to be particularly effective. Polyethylene tubing has several advantages over stainless steel cannulas, in particular it is inexpensive and readily available in a wide range of internal diameters, easily cleaned and dried, and allows visible transfer of reagents under inert gas pressure with blockages readily removed by flexing the tube.

Methyllithium, MeLi

(i) <u>from Methyliodide and Lithium.</u>[6]

To a suspension of lithium chips (0.118gm, 17mmol) in anhydrous diethyl ether (40cm^3) under a nitrogen atmosphere was added iodomethane (0.55cm^3, 8.5mmol) in anhydrous diethyl ether (20cm^3) over *ca.* 30 minutes. The suspension was stirred until the lithium had been consumed or the reaction had ceased, as evidenced by dulling of the lithium surface, followed by standardisation with 1,3-diphenyltosylhydrazone. Yields of methyllithium were commonly in the range 40-50%, and solutions were used immediately.

(ii) <u>Halide-free MeLi, from Methylchloride and Lithium (1% Na).</u>[7]

The basic procedure as reported by House *et al.*[7] was followed except for the use of lithium shot (containing 1% Na) in place of lithium dispersion (1% Na), and the requirement that the reaction vessel be cooled in an ice-bath to maintain reaction temperatures of *ca.* 25°C and reaction times of *ca.* 1.5 hours. Yields of methyllithium

prepared using lithium shot (1% Na, particle size < 1mm) were ~20% lower than those reported by House, undoubtedly due to the larger lithium particle size. Lithium dispersion containing low sodium content gave methyllithium yields of only *ca.* 20% of those reported. The dependence of yield of organolithium reagents on sodium content is well known and has been documented.[8]

Lithium shot was prepared under an **argon** atmosphere by vigorous stirring of molten lithium wire suspended in paraffin oil at 220°C, and allowing the oil to cool slowly to 150°C with stirring maintained throughout this cooling period. The oil was cooled further to 60-70°C and was syphoned off. The residual lithium was washed with several 50cm^3 portions of anhydrous hexane, followed by anhydrous diethyl ether. The size of the lithium shot is critically dependent on the use of vigorous stirring and the lithium : paraffin oil ratio; particle sizes of less than 1 mm diameter were produced when *ca.* 7gm of lithium wire was heated in 400cm^3 of paraffin oil with use of a mechanical stirrer.

n-Butyllithium, Bu^{n}Li.[6,9]

To a suspension of lithium chips (6.27gm, 0.9mol) in anhydrous diethyl ether (200cm^3) under a nitrogen atmosphere was added neat 1-bromobutane (0.5cm^3), and the mixture allowed to stir until initiation of reaction had occurred. The suspension was then cooled in an acetone/CO_2 bath so that the reaction temperature was *ca.* -10°C, 1-bromobutane (39cm^3, 0.36mol) in anhydrous diethyl ether (40cm^3) was added dropwise over a 30 minute period with continued cooling by the acetone/CO_2 bath so that the reaction temperature remained in the range -10→-5°C; bath temperatures of -40→-50°C were generally required. After addition was complete and the remaining lithium chips had lost their shiny surface, the mixture was allowed to stir for one hour while warming slowly to *ca.* 10°C. Titration of the solution gave concentrations in the range 0.9-1.1 molar, *i.e.* 66-76% yield. Solutions stored at -20°C remain active for several weeks but require titration immediately prior to use.

Phenyllithium, PhLi.[6,9]

To a suspension of lithium chips (1.2gm, 0.18mol) in anhydrous diethyl ether ($50cm^3$) under a nitrogen atmosphere was added neat bromobenzene ($0.5cm^3$), and the mixture heated gently until initiation of reaction had occurred. Bromobenzene ($9.5cm^3$, 0.09mol) in anhydrous diethyl ether ($10cm^3$) was then added dropwise over a period of 15-30 minutes at such a rate that reflux was maintained throughout the whole addition. This was followed by reflux for 1 1/2-2 hours; little or no lithium metal should remain at this stage. Yields were consistently in the rage 95-100% and titration was found not to be necessary.

2-Pyridyllithium pyLi.[10]

To a cooled (-50°C) solution of phenyllithium (Li:3.03gm, bromobenzene:$23cm^3$) in anhydrous diethyl ether ($150cm^3$) was added dropwise 2-bromopyridine ($21cm^3$, 0.22mol) in anhydrous diethyl ether ($30cm^3$) and the resulting mixture stirred for 30 minutes while maintaining the temperature between -40→-50°C. Yields of 2-pyridyllithium were in the range 70-85% and the red solutions produced were used immediately.

Potassium pyrazolide, Kpz.

To a suspension of potassium (5.0gm, 0.13mol) in anhydrous tetrahydrofuran ($100cm^3$) was added pyrazole (9.0gm, 0.13mol), and the mixture was refluxed until all the potassium metal had been consumed, *ca.* 1 1/2 hours. The yield is quantitative and the white suspension formed was used immediately.

Bis(pyrazol-1-yl)methanone, pz_2CO.[11]

To a cooled (-50°C), freshly prepared suspension of sodium pyrazolide (prepared from Na:6.9gm and pz:20gm in an identical fashion to that for Kpz above) was added phosgene ($COCl_2$, $78cm^3$, 0.15mol). The suspension was allowed to warm slowly to room temperature, followed by gentle refluxing overnight. Next day, the suspension was rapidly filtered through a frit, and the residue washed with several portions of anhydrous diethyl ether. Evaporation of the filtrate, and cooling to 0°C

afforded the desired product in near quantitative yield. The product, pz_2CO, is sensitive to both air and water, and was stored under nitrogen until required.

6.2.3 Preparation of Organopalladium(II) Precursors.

During the course of this study the following dimethyl- and monomethylhalopalladium(II) complexes were prepared and were subsequently found to be excellent precursors for the preparation of dimethyl- and monomethylpalladium(II) complexes with a wide range of donor ligands.

Dimethyl(μ-pyridazine-N,N')palladium(II), $\{PdMe_2(\mu\text{-pyridazine})\}_n$.

To a cooled (-60°C) suspension of *trans*-$\{PdCl_2(SMe_2)_2\}$ (1.5gm, 5.0mmol) in anhydrous diethyl ether (130cm^3) under a nitrogen atmosphere was added halide-free methyllithium (11.9cm^3, 10.3mmol). The resulting mixture was allowed to stir at -60→-30°C until a clear colourless solution was obtained with no unreacted *trans*-$\{PdCl_2(SMe_2)_2\}$ evident. To this solution was added pyridazine (0.38cm^3, 5.2mmol) in diethyl ether (10cm^3), followed by hydrolysis at *ca.* -15°C, and rapid filtration. The yellow orange solid was washed with water and several portions of diethyl ether, dried immediately under high vacuum at ambient temperature, and stored at -20°C until required {7.5-8.5 gm, 70-80%; m pt. *ca.* 80°C (decomp.)}.

^{1}H N.M.R., Acetone-D6;

9.23, m, $H_{3,6}$, 2H; 7.98, m, $H_{4,5}$, 2H; 0.06, s, Pd**Me**, 6H.

***trans*-Di-μ-chloro-bis{(dimethylsulphide)methylpalladium(II)}, *trans*-$\{PdMe(\mu\text{-}Cl)(SMe_2)\}_2$.**

To a cooled (-70°C) suspension of *trans*-$\{PdCl_2(SMe_2)_2\}$ (0.69gm, 2.3mmol) in anhydrous diethyl ether (70cm^3) under a nitrogen atmosphere was added halide-free methyllithium (1.85cm^3, 2.3mmol). The suspension was stirred for one hour at -60→-50°C to give a colourless solution with some unreacted starting material. Gradual warming to -15°C gave an orange solution with little unreacted *trans*-

{$PdCl_2(SMe_2)_2$}. Hydrolysis and filtration at *ca.* -15°C and subsequent evaporation of solvent in a vacuum at 0°C gave a black solid. Extraction of the solid with dry acetone (4x5cm^3) followed by addition of hexane (20cm^3), and slow evaporation at 0°C, afforded the product {0.22gm, 45%; m.pt. 87°C (decomp)}. Recrystallisation was found not to be necessary, but may be achieved using acetone-light petroleum ether or acetone-water.

Analysis;

found% : C 16.6 H 3.7

calc.% : C 16.5 H 4.1

^{1}H N.M.R., Acetone-D6;

2.34, s, SMe, 6H; 0.78, s, PdMe, 3H.

Molecular weight, $CHCl_3$, 37°C;

found : 448

calc. : 438

Infrared;

near : 2952(mw), 2912(mw), 2880(mw), 1428(s), 1320(mw), 1304(mw), 1154(m), 1034(m), 988(m), 750(m), 537(w).

far : 319(w), 275(s), 244(s), 285(w), 211(s), 155(vw), 141(vw), 105(vw) cm^{-1}.

***trans*-Di-μ-bromo-bis{(dimethylsulphide)methylpalladium(II)}, *trans*-{PdMe(μ-Br)(SMe_2)}$_2$.**

A procedure similar to that described above, using *trans*-{$PdBr_2(SMe_2)_2$}, afforded the desired product {70%; m.pt. 104-105°C (decomp.)}. Recrystallisation was not necessary but may be achieved using acetone-petroleum ether (40-60).

Analysis;

found% : C 13.8 H 3.4

calc. % : C 13.7 H 3.4

^{1}H N.M.R., Acetone-D6;

2.43, s, SMe, 6H; 0.87, s, PdMe, 3H.

Molecular Weight, $CHCl_3$, 37°C;

found : 584

calc. : 527

Infrared;

near : 2988(m), 2912(m), 2892(mw), 1428(s), 1316(m), 1152(m), 1028(m), 986(s) 762(mw), 537(mw).

far : 319(w), 175(s), 157(m), 288(mw), 195(m), 134(w), 119(vw), 105(w) cm^{-1}.

***trans*-Di-μ-iodo-bis{(dimethylsulphide)methylpalladium(II)}, $\{PdMe(\mu\text{-}I)(SMe_2)\}_2$.**

A similar procedure to that described above using *trans*-$\{PdCl_2(SMe_2)_2\}$ and one mole equivalent of methyllithium (Li:0.118gm, MeI:0.55cm^3) gave an orange solution after hydrolysis with little or no reduced palladium present. After filtration, water (30cm^3) was added and diethyl ether removed in a vacuum at 0°C to give the desired product {85%; m.pt. 120°C (decomp.)}, which did not require recrystallisation.

Analysis;

found % : C 11.9 H 2.8

calc. % : C 11.6 H 2.9

^1H N.M.R, Acetone-D6;

2.39, s, S**Me**, 6H; 0.93, s, Pd**Me**, 3H.

Molecular weight, $CHCl_3$, 37°C;

found : 679

calc. : 621

Infrared;

near : 2976(mw), 2908 (mw), 1414 (m),1320(m), 1302(mw), 1142(m), 1028(m), 980(m), 753(mw), 522(w).

far : 309(w), 150(s), 280(mw), 188(w), 126(w), 111(w) cm^{-1}.

Synthesis of $\{PdMe(\mu\text{-}X)(SMe_2)\}_2$(X=Br, I).

(i) from Halide-free Methyllithium and Halogenomethane (MeX).

To a cooled (-60°C) suspension of *trans*-$\{PdCl_2(SMe_2)_2\}$ (0.417gm, 1.4mmol) in anhydrous diethyl ether (70cm^3) under a nitrogen atmosphere was added halide-free methyllithium (3.5cm^3, 2.9mmol). The suspension was allowed to stir at -60→-50°C for one hour to give a clear, colourless solution free from unreacted reagent. This was followed by warming to *ca.* -40°C, addition of iodomethane (0.5cm^3, 8mmol), and gradual warming to -15°C to give a yellow solution. Hydrolysis (20cm^3), followed by filtration and evaporation of diethyl ether at 0°C in a vacuum gave $\{PdMe(\mu\text{-}I)(SMe_2)\}_2$ (0.39gm, 91%).

A similar procedure which involved bubbling bromomethane into the clear colourless solution obtained above gave a black suspension at 0°C. Hydrolysis (20cm^3), followed by filtration gave a yellow solution which upon evaporation of diethyl ether at 0°C afforded the product $\{PdMe(\mu\text{-}Br)(SMe_2)\}_2$ (41%).

(ii) from $\{PdMe(\mu\text{-}Cl)(SMe_2)\}_2$ and KX.

To a suspension of $\{PdMe(\mu\text{-}Cl)(SMe_2)\}_2$ in diethyl ether at room temperature was added an aqueous solution of KX (X=Br or I), and the resulting suspension allowed to stir for 0.5 hours. Evaporation of diethyl ether at 0°C in a vacuum afforded the desired products which were isolated by filtration.

6.3 PREPARATION OF $Me_2Pd(II)$ COMPLEXES

6.3.1 From Halide-free Methyllithium and *trans*-$\{PdCl_2(SMe_2)_2\}$.

To a cooled (-60°C) suspension of *trans*-$\{PdCl_2(SMe_2)_2\}$ (1.5gm, 5.0 mmol) in anhydrous diethyl ether (280cm^3) under a nitrogen atmosphere was added halide-free methyllithium (16cm^3, 11.0mmol). The suspension was stirred at -60→-40°C until a clear colourless solution free from unreacted *trans*-$\{PdCl_2(SMe_2)_2\}$ had formed, followed by addition of solid 2,2-bis(pyrazol-1-yl)propane, pz_2CMe_2,

(0.87gm, 5.0mmol) at -60°C, and gradual warming to -15°C. Hydrolysis ($2cm^3$) filtration, separation and drying of the organic phase ($MgSO_4$), and slow removal of diethyl ether at 0°C in a vacuum to half the original volume, followed by addition of hexane ($30cm^3$), and further removal of diethyl ether at 0°C gave a white crystalline solid. The solid formed was collected by filtration, washed with cold (0°C) diethyl ether ($10cm^3$), followed by hexane ($10cm^3$), and dried under high vacuum. The filtrate plus washings were evaporated further to yield another crop of white solid, which was treated as above. The product formed, $\{PdMe_2(pz_2CMe_2)\}$ {1.17gm, 75%; m.pt. 85°C (decomp).}, could be recrystallised with difficulty from acetone/hexane at -70°C, however, the first crop of solid isolated was found to be microanalytically pure.

Analysis;

found %	: C	42.20	H	5.87	N	17.33
calc. %	: C	42.25	H	5.80	N	17.92

^1H N.M.R., Acetone-D6;

Ambient : 8.16, dd, H_5 ($^3J_{4,5}$=2.74, $^4J_{3,5}$=0.77Hz), 2H; 7.67, dd, H_3 ($^3J_{3,4}$=1.94, $^4J_{3,5}$=0.70 Hz), 2H; 6.40, dd, H_4 ($^3J_{3,4}$=2.10, $^3J_{4,5}$=2.68 Hz), 2H; 2.75, s, C**Me**, 6H; 0.09, s, Pd**Me**, 6H.

low, -60°C : pyrazole and methylpalladium resonances as above;
2.86, s, C**Me** (ax), 3H; 2.62, s, C**Me** (eq), 3H;
coalescence temperature=-20°C.

An identical procedure to that outlined above was employed for the following ligands:

(i) **Bis(pyrazol-1-yl)methane, pz_2CH_2,**

$\{PdMe_2(pz_2CH_2)\}$ formed in 56% yield; m.pt. 90°C (decomp.).

The complex was unstable and not amenable to recrystallisation, consequently a correct microanalysis could not be obtained. However, reaction of $\{PdMe_2(pz_2CH_2)\}$

with 1,2-bis(diphenylphosphino)ethane, dppe, gave white {$PdMe_2$(dppe)} which had an identical ^{1}H N.M.R. spectrum to that for {$PdMe_2$(dppe)} prepared using literature methods[14].

^{1}H N.M.R. Acetone-D6;

Ambient : 8.02, d, H_5($^3J_{4,5}$=2.37 Hz), 2H; 7.65, d, H_3 ($^3J_{3,4}$=1.72 Hz), 2H; 6.71, s, CH, 2H; 6.40, *pseudo* t, H_4 ($^3J_{4,(3,5)}$=2.13 Hz), 2H; 0.11, s, PdMe, 6H.

low, -30°C : pyrazole and methylpalladium resonances as above; 6.89, d, CH (eq) (^2J=14.11 Hz), 1H; 6.58, d, CH (ax) (^2J=14.07 Hz), 1H;

coalescence temperature=-10°C.

(ii) 1,1-Bis(pyrazol-1-yl)ethane, pz_2CHMe.

{$PdMe_2$(pz_2CHMe)} formed in 61% yield; m.pt. 105°C (decomp).

Analysis;

found %	: C	40.69	H	5.58	N	18.90
calc. %	: C	40.22	H	5.40	N	18.76

^{1}H N.M.R., Acetone-D6;

Ambient : 8.09, d, H_5 ($^3J_{4,5}$=2.80 Hz), 2H; 7.66, d, H_3 ($^3J_{3,4}$=1.90 Hz), 2H; 7.16, q, CH (^3J=6.75Hz), 1H; 6.40, *pseudo* t, H_4 ($^3J_{4,(3,5)}$=2.21Hz), 2H; 2.53, d,CMe (^3J=6.76 Hz), 3H; 0.11, s, PdMe, 6H.

low, -30°C : *isomer A*, 8.06, d, H_5 ($^3J_{4,5}$=2.42 Hz), 2H; 7.69, d, H_3 ($^3J_{3,4}$=1.92 Hz), 2H; 7.25, q, CH (eq) (^3J=6.75Hz),1H; 6.41, *pseudo* t, H_4 ($^3J_{4,(3,5)}$=2.36 Hz), 2H; 2.54, d, CMe (ax) (^3J=6.73 Hz), 3H; 0.08, s, PdMe, 6H.

isomer B, 8.20, d, H_5 ($^3J_{4,5}$=2.70 Hz), 2H; 7.62, d, H_3 ($^3J_{3,4}$=1.82 Hz), 2H; 7.03, q, CH (ax) (^3J=7.03 Hz), 1H; 6.44, *pseudo* t, H_4 ($^3J_{4,(3,5)}$=2.27 Hz) 2H; 2.46, d, CMe (eq) (^3J=6.96 Hz), 3H; 0.06, s, PdMe, 6H.

Isomer A and *B* in *ca.* 2:1 ratio; coalescence temperature=-8°C.

(iii) Tris(pyrazol-1-yl)methane, pz_3CH.

{$PdMe_2(pz_3CH)$} formed in 72% yield; m.pt. 130°C (decomp.).

Analysis;

found% : C 41.38 H 4.76 N 23.96

calc. % : C 41.10 H 4.60 N 23.96

^{1}H N.M.R., Acetone-D6;

Ambient : 9.14, s, CH, 1H, 8.47, s, H_5, 3H; 7.77, s, H_3, 3H; 6.33, s, H_4, 3H; 0.09, s, PdMe, 6H.

low, -70°C : *free pyrazole,* 8.78, d, H_5 ($^3J_{4,5}$=2.43 Hz), 1H; 7.64, s, H_3, 1H; 6.43, s, H_4, 1H.

bound pyrazole, 8.50, d, H_5 ($^3J_{4,5}$=2.42 Hz), 2H; 7.92, s, H_3, 2H; 6.64, s, H_4, 2H.

9.45, s, CH, 1H; 0.05, s, PdMe, 6H.

(iv) Tetrakis(pyrazol-1-yl)methane, pz_4C.

{$PdMe_2(pz_4C)$} formed in 60% yield; m.pt. 130°C (decomp.).

Analysis;

found % : C 42.97 H 4.35 N 26.88

calc. % : C 43.23 H 4.35 N 26.89

^{1}H N.M.R., Acetone-D6;

Ambient : 7.93, s, H_3, 4H; 7.25, s, H_5, 3H; 6.75, s, H_5, 3H; 6.60, s, H_4, 4H; -0.07, s, PdMe, 6H.

low, -70°C : *bound pyrazole, ring A,* 8.19, d, H_3 ($^3J_{3,4}$=1.36 Hz), 1H; 6.70, *pseudo* t, H_4 ($^3J_{4,(3,5)}$=2.34 Hz), 1H; 6.56, d, H_5 ($^3J_{4,5}$=2.66 Hz), 1H.

ring B, 8.07, d, H_3 ($^3J_{3,4}$=1.50 Hz), 1H; 7.21, d, H_5 ($^3J_{4,5}$=2.82 Hz), 1H; 6.72, *pseudo* t, H_4 ($^3J_{4,(3,5)}$=2.44 Hz), 1H.

free pyrazole, ring C, 7.90, d, H_3 ($^3J_{3,4}$=1.38 Hz), 1H; 7.45, d, H_5 ($^3J_{4,5}$=2.81 Hz), 1H, 6.60, *pseudo* t, H_4 ($^3J_{4,(3,5)}$=2.41 Hz), 1H.

ring D; 7.83, d, H_3 ($^3J_{3,4}$=1.35 Hz), 1H; 6.92, d, H_5($^3J_{4,5}$=2.60 Hz), 1H; 6.64, *pseudo* t, H_4 ($^3J_{4,(3,5)}$=2.17 Hz), 1H.

-0.10, s, PdMe, 3H; -0.14, s, PdMe, 3H.

(v) 2,2'-bipyridyl, bipy.[12]

{$PdMe_2$(bipy)} formed in 82% yield.

^{1}H N.M.R., Acetone-D6;

8.87, ddd, H_6 ($^3J_{5,6}$=5.26, $^4J_{4,6}$=1.64, $^5J_{3,6}$=0.78 Hz), 2H; 8.46, m, H_3 ($^3J_{3,4}$=8.10, $^4J_{3,5}$~1 Hz), 2H; 8.27, ddd, H_4 ($^3J_{3,4}$=8.11, $^3J_{4,5}$=7.56, $^4J_{4,6}$=1.70 Hz), 2H; 7.69, ddd, H_5 ($^3J_{4,5}$=7.56, $^3J_{5,6}$=5.25, $^4J_{3,5}$=1.23 Hz), 2H; 0.24, s, PdMe, 6H.

(vi) 1,2-Di(methylthio)ethane, $MeSCH_2CH_2SMe$.[12]

{$PdMe_2$($MeSCH_2CH_2SMe$)} formed in 65% yield.

^{1}H N.M.R., Acetone-D6;

2.96, s, SCH_2 , 4H; 2.27, s, SMe, 6H; 0.12, s, PdMe, 6H.

6.3.2 From {$PdMe_2$(μ-pyridazine)}$_n$ with Addition of Ligands

To solid orange {$PdMe_2$(μ-pyridazine)}$_n$ (0.40gm, 1.85mmol) was added with stirring a benzene solution (20cm^3) of bis(pyridin-2-yl)methane, py_2CH_2, (0.32gm, 1.90mmol) to yield a clear slightly yellow solution. Filtration, followed by evaporation of benzene at room temperature in a vacuum to *ca.* 20cm^3, and addition of hexane (10-20cm^3) gave a white crystalline solid. The solid formed was collected by filtration, washed with cold (0°C) diethyl ether (10cm^3), followed by hexane (10cm^3), and dried under high vacuum. The product {$PdMe_2$(py_2CH_2)} {0.40gm, 71%; m.pt. 140°C (decomp.)}, did not require recrystallisation.

Analysis;

found %	: C	50.53	H	5.23	N	9.16
calc. %	: C	50.91	H	5.26	N	9.13

^{1}H N.M.R., Acetone-D6;

Ambient : 8.61, ddd, H_6 ($^3J_{5,6}$=5.29, $^4J_{4,6}$=1.64, $^5J_{3,6}$=0.78 Hz), 2H; 7.88, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.67, $^4J_{4,6}$=1.72 Hz), 2H; 7.64, m, H_3 ($^3J_{3,4}$~8, $^4J_{3,5}$~1Hz), 2H; 7.38, ddd, H_5 ($^3J_{4,5}$=7.56, $^3J_{5,6}$=5.38, $^4J_{3,5}$=1.35 Hz), 2H; 4.61, s b, **CH**, 2H; 0.12, s, Pd**Me**, 6H.

low, -40°C : pyridine resonances as above;
4.68, d, CH (eq) (^{2}J=13.11 Hz), 1H; 4.52, d, CH (ax) (^{2}J=13.15 Hz);
coalescence temperature=0°C.

A procedure similar to that described above using acetone or benzene solvent, as indicated, was employed for the preparation of dimethylpalladium(II) complexes with the following ligands:

(i) 1,1-Bis(pyridin-2-yl)ethane, py_2CHMe.

{$PdMe_2(py_2CHMe)$} prepared in benzene in 65% yield; m.pt.130°C (decomp.).

Analysis;

found %	: C	52.67	H	5.45	N	8.66
calc %	: C	52.43	H	5.66	N	8.74

^{1}H N.M.R., Acetone-D6;

high, 50°C : 8.68, d, H_6 ($^3J_{5,6}$~4.8 Hz), 2H; 7.87, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.73, $^4J_{4,6}$=1.70 Hz), 2H; 7.58, m, H_3 ($^3J_{3,4}$~7.9 Hz); 7.34, ddd, H_5 ($^3J_{4,5}$=7.52, $^3J_{5,6}$=5.36, $^4J_{3,5}$=1.36 Hz), 2H; ~5.2, s, CH, 1H; ~2.4, s, **CMe**, 3H; 0.14, s, Pd**Me**, 6H.

low, -10°C : *isomer A*, 5.26, q, CH (ax) (^{2}J=7.46 Hz), 1H; 1.95, d, **CMe** (eq) (^{2}J=7.46 Hz), 3H.
isomer B, 4.70 q, CH (eq) (^{2}J=7.20 Hz), 1H; 2.45, d, **CMe** (ax) (^{2}J=7.20 Hz), 3H.

isomer A and B, 8.69, d, H_6 ($^3J_{5,6}$=5.4 Hz), 1H; 8.59, d, H_6 ($^3J_{5,6}$=5.20 Hz), 1H; 7.92, m, H_4, 2H; 7.63, m, H_3, 2H; 7.40, m, H_5, 2H; 0.11, s, PdMe, 3H; 0.09, s, PdMe, 3H.

Isomer A and B in 7:8 ratio.

ambient : as for -10°C with all resonances broad and no structure discernible.

(ii) 2,2-Bis(pyridin-2-yl)propane, py_2CMe_2.

{$PdMe_2(py_2CMe_2)$} prepared in benzene in 62% yield; m.pt. 155°C (decomp.).

Analysis;

found %	: C	53.75	H	5.93	N	8.61
calc. %	: C	53.82	H	6.02	N	8.37

^{1}H N.M.R., Acetone-D6;

Ambient : 8.78, dd, H_6 ($^3J_{5,6}$=5.23, $^4J_{4,6}$=1.88 Hz), 2H; 7.89, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.85, $^4J_{4,6}$=1.86 Hz), 2H; 7.73, d, H_3 ($^3J_{3,4}$=7.81 Hz), 2H; 7.34, m, H_5, 2H; ~3.0, s (obs.), CMe (ax), 3H; ~2.2, s (obs.), CMe (eq), 3H; 0.14, s, PdMe, 6H.

low, -10°C : pyridine and methylpalladium resonances as above;
2.84, s, CMe (ax), 3H; 2.22, s, CMe (eq), 3H;
coalescence temperature *ca.* 35°C.

(iii) 1,1-Bis(pyridin-2-yl)ethene, $py_2C{=}CH_2$.

{$PdMe_2(py_2C{=}CH_2)$} prepared in benzene in 52% yield; m.pt. 160°C (decomp.).

Analysis;

found %	: C	49.51	H	5.04	N	9.64
calc. %	: C	52.76	H	5.06	N	9.79

^{1}H N.M.R., Acetone-D6;

8.66, ddd, H_6 ($^3J_{5,6}$=5.33, $^4J_{4,6}$=1.64, $^5J_{3,6}$=0.77 Hz), 2H; 7.99, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.74, $^4J_{4,6}$=1.68 Hz), 2H; 7.73, m, H_3 ($^3J_{3,4}$~7.8 Hz), 2H; 7.49, ddd, H_5 ($^3J_{5,6}$=5.37, $^3J_{4,5}$=7.68, $^4J_{3,5}$=1.31 Hz), 2H; 6.00, s, C=CH_2, 2H; 0.01, s, Pd**Me**, 6H.

(iv) Tris(pyridin-2-yl)methane, py_3CH.

{$PdMe_2(py_3CH)$} prepared in acetone in 25% yield; m.pt. 160°C (decomp.).

Analysis;

found %	: C	55.86	H	4.96	N	10.72
calc. %	: C	56.34	H	4.99	N	10.95

^{1}H N.M.R., Acetone-D6;

Ambient : 8.59, d, H_6 ($^3J_{5,6}$=4.34 Hz), 3H; 7.86, *pseudo* t, H_4, 3H; 7.61, s, H_3, 3H; 7.36, m, H_5, 3H; 6.08, s, **CH**, 1H; -0.20, s, Pd**Me**, 6H.

low, -70°C : *free pyridine*, 8.35, d, H_6 ($^3J_{5,6}$~4 Hz), 1H; 7.64, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.7, $^4J_{4,6}$=1.76 Hz), 1H; 7.20, m, H_5, 1H; 6.81, d, H_3 ($^3J_{3,4}$~7.9 Hz), 1H.

bound pyridine, 8.66, d, H_6($^3J_{5,6}$~4 Hz), 2H; 8.06, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.6, $^4J_{4,6}$=1.66 Hz), 2H; 7.95, d, H_3 ($^3J_{3,4}$~7.6 Hz), 2H; 7.51, m, H_5, 2H.

6.19, s, **CH**, 1H; -0.03, s, Pd**Me**, 6H.

(v) Bis(N-methylimidazol-2-yl)methane, mim_2CH_2.

{$PdMe_2(mim_2CH_2)$} prepared in acetone in 79% yield; m.pt. 190°C (decomp.).

Analysis;

found %	: C	42.76	H	5.93	N	16.19
calc.	: C	42.25	H	5.80	N	17.92[1]

^{1}H N.M.R., Dimethylsulphoxide-D6;

7.26, d, $H_{4(5)}$ ($^3J_{4,5}$=1.39 Hz), 2H; 6.96, d, $H_{5(4)}$ ($^3J_{4,5}$=1.37 Hz), 2H; 4.26, s, CH_2, 2H; 3.80, s, N**Me**, 6H; -0.09, s, Pd**Me**, 6H.

(vi) Bis(N-methylimidazol-2-yl)methanone, mim_2C0.

{$PdMe_2(mim_2C0$} prepared in acetone in 78% yield; m.pt. 190°C (decomp.).

Analysis;

found %	: C	39.54	H	4.96	N	17.68
calc. %	: C	40.44	H	4.94	N	17.15

^{1}H N.M.R., Acetone-D6;

7.59, d, $H_{4(5)}$ ($^3J_{4,5}$=1.21 Hz) 2H; 7.39, d, $H_{5(4)}$ ($^3J_{4,5}$=1.19 Hz), 2H; 4.17, s, N**Me**, 6H; 0.10, s, Pd**Me**, 6H.

Infrared;

1634, 1296, 1168, 1064, 902, 848, 812, 790, 724.cm^{-1}.

(vii) 1,1-Bis(N-methylimidazol-2-yl)ethane, mim_2CHMe.

{$PdMe_2(mim_2CHMe)$} prepared in acetone in 49% yield; m.pt.160°C (decomp.).

Analysis;

found %	: C	43.73	H	6.05	N	17.03
calc. %	: C	44.12	H	6.20	N	17.15

^{1}H N.M.R., Acetone-D6;

7.03, d, $H_{4(5)}$ ($^3J_{4,5}$=1.40 Hz), 2H; 6.96, d, $H_{5(4)}$ ($^3J_{4,5}$=1.42 Hz), 2H; 4.68, q, CH (eq) (^3J=7.00 Hz), 1H; 3.86, s, N**Me**, 6H; 1.70, d, **CMe** (ax) (^3J=7.01 Hz), 3H; -0.02, s, Pd**Me**, 6H.

Spectra remain unchanged to -70°C.

(viii) 1,1-Bis(N-methylimidazol-2-yl)ethene, $mim_2C{=}CH_2$.

{$PdMe_2(mim_2C{=}CH_2)$} prepared in acetone in 61% yield; m.pt. 185°C (decomp.).

Analysis;

found %	: C	44.30	H	5.51	N	17.13
calc %	: C	44.39	H	5.59	N	17.25

^{1}H N.M.R., Acetone-D6;

7.20, d, $H_{4(5)}$ ($^3J_{4,5}$=1.36 Hz), 2H; 7.05, d, $H_{5(4)}$ ($^3J_{4,5}$=1.40 Hz), 2H; 6.16, s, C=CH_2, 2H; 3.92, s, N**Me**, 6H; -0.03, s, Pd**Me**, 6H.

(ix){(pyridin-2-yl)(N-methylimidazol-2-yl)}methane, pymimCH_2.

{$PdMe_2$(pymimCH_2)} prepared in acetone in 69% yield; m.pt. 120°C (decomp.).

Analysis;

found %	: C	46.15	H	5.39	N	13.36
calc. %	: C	46.54	H	5.53	N	13.57

^{1}H N.M.R., Acetone-D6;

pyridine resonances, 8.65, dd, H_6 ($^3J_{5,6}$=5.38, $^4J_{4,6}$~1.3 Hz), 1H; 7.90, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.64, $^4J_{4,6}$=1.75 Hz), 1H; 7.68, d, H_3 ($^3J_{3,4}$=7.64 Hz), 1H; 7.42, ddd, H_5 ($^3J_{5,6}$=5.38, $^3J_{4,5}$=7.60, $^4J_{3,5}$=1.28 Hz), 1H;

N-methylimidazole resonances, 7.11, d, $H_{4(5)}$ ($^3J_{4,5}$=1.41 Hz), 1H; 6.88, d, $H_{5(4)}$ ($^3J_{4,5}$=1.43 Hz), 1H; 3.86, s, N**Me**, 3H;

4.34, s, CH_2, 2H; 0.07, s, Pd**Me** *trans* to py,3H; -0.07, s, Pd**Me** *trans* to mim, 3H.

Spectra remain unchanged to -70°C.

(x) 1,1-{(pyridin-2-yl)(N-methylimidazol-2-yl)}ethane, pymimCHMe.

{$PdMe_2$(pymimCHMe)} prepared in acetone in 59% yield; m.pt. 140°C (decomp.).

Analysis;

found %	: C	47.90	H	5.81	N	12.72
calc. %	: C	48.24	H	5.92	N	12.98

^{1}H N.M.R., Acetone-D6;

pyridine resonances, 8.76, dd, H_6 ($^3J_{5,6}$=5.14, $^4J_{4,6}$~1.4 Hz), 1H; 7.87, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.64, $^4J_{4,6}$=1.8 Hz),, 1H; 7.60, m, H_3 ($^3J_{3,4}$=7.82 Hz), 1H; 7.36, m, H_5, 1H;

N-methylimidazole resonances, 7.18, d, $H_{4(5)}$ ($^3J_{4,5}$=1.43 Hz), 1H; 6.92, d, $H_{5(4)}$ ($^3J_{4,5}$=1.42 Hz), 1H; 3.86, s, **NMe**, 3H;

4.71, q, CH (eq) (^3J=7.09 Hz), 1H; 2.14, d, **CMe** (ax) (^3J=7.08 Hz), 3H; 0.11, s, Pd**Me** *trans* to py, 3H; -0.03, s, Pd**Me** *trans* to mim, 3H.

Spectra remain unchanged to -70°C.

(xi) 1,1-{(pyridin-2-yl)(N-methylimidazol-2-yl)ethene, pymimC=CH_2,

{$PdMe_2$(pymimC=CH_2)} prepared in acetone in 52% yield; m.pt. 155°C (decomp.).

Analysis;

found %	: C	48.52	H	5.25	N	12.61
calc. %	: C	48.54	H	5.33	N	13.06

^{1}H N.M.R., Acetone-D6;

pyridine resonances, 8.72, d, H_6 ($^3J_{5,6}$=5.28 Hz), 1H; 7.98, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.7, $^4J_{4,6}$=1.65 Hz), 1H; 7.78, d, H_3 ($^3J_{3,4}$=7.83 Hz) 1H; 7.45, ddd, H_5 ($^3J_{5,6}$=5.36, $^3J_{4,5}$=7.66, $^3J_{3,5}$=1.35 Hz), 1H.

N-methylimidazole resonances, 7.25, d, $H_{4(5)}$ ($^3J_{4,5}$=1.32 Hz), 1H; 7.03, d, $H_{5(4)}$ ($^3J_{4,5}$=1.32 Hz), 1H; 3.88, s, **NMe**, 3H.

6.25, s, C=CH *trans* to py, 1H; 6.01, s, C=CH *trans* to mim,1H; 0.08, s, Pd**Me** *trans* to py, 3H; -0.10, s, Pd**Me** *trans* to mim, 3H.

(xii) {(Pyridin-2-yl)(N-methylimidazol-2-yl)methanone, pymimC0.

{$PdMe_2$(pymimC0)} prepared in acetone in 46% yield; m.pt.150°C (decomp.).

Analysis;

found %	: C	44.13	H	4.62	N	12.81
calc. %	: C	44.53	H	4.67	N	12.98

^{1}H N.M.R., Acetone-D6;

pyridine resonances, 8.89, dd, H_6 ($^3J_{5,6}$=5.43, $^4J_{4,6}$~1 Hz). 1H; 8.22; m, $H_{3,4}$, 2H; 7.76, ddd, H_5 ($^3J_{5,6}$=5.26, $^3J_{4,5}$=7.80, $^4J_{3,5}$=1.90 Hz), 1H.

N-methylimidazole resonances, 7.63, d, $H_{4(5)}$ ($^3J_{4,5}$=1.09 Hz), 1H; 7.32, d, $H_{5(4)}$ ($^3J_{4,5}$=1.08 Hz), 1H; 4.10, s, NMe, 3H.

0.12, s, PdMe *trans* to py, 3H; -0.01, s, PdMe*trans* to mim, 3H.

Infrared;

1640, 1584, 1264, 1248, 1172, 1152, 918, 768, 618 cm^{-1}

(xiii){(Pyridin-2-yl)(pyrazol-1yl)}methane, pypzCH_2

{$PdMe_2$(pypzCH_2)} prepared in benzene in 54% yield; m.pt.135°C (decomp.).

Analysis;

found %	: C	44.61	H	5.01	N	14.12
calc %	: C	44.69	H	5.11	N	14.21

^{1}H N.M.R., Acetone-D6;

Ambient : *pyridine resonances*, 8.69, dd, H_6 ($^3J_{5,6}$=5.20, $^4J_{4,6}$=1.41 Hz), 1H; 7.97, m, H4, 1H; 7.70, d, H_3 ($^3J_{3,4}$=7.65 Hz), 1H; 7.51, ddd, H_5 ($^3J_{4,5}$=7.82, $^3J_{5,6}$=5.40, $^4J_{3,5}$=1.24 Hz), 1H.

pyrazole resonances, 7.97, m, H_5, 1H; 7.57, d, H_3 ($^3J_{3,4}$=1.60), 1H; 6.34, *pseudo* t, H_4 ($^3J_{4,(3,5)}$=2.24 Hz), 1H.

5.71, s, CH_2, 2H; 0.14, s, PdMe, 3H; 0.08, s, PdMe, 3H.

Low, -60°C: methylpalladium, pyrazole and pyridine ring protons as above;

5.82, d, CH (eq) (^3J=14.35 Hz), 1H; 5.64, d, CH (ax) (^3J=14.44 Hz), 1H.

(xiv){(Pyrazol-2-yl)(N-methylimidazol-2-yl)}methane,pzmimCH_2

{$PdMe_2$(pzmimCH_2)} prepared in acetone in 54% yield; m.pt. 135°C (decomp.).

Analysis;

found %	: C	40.22	H	5.40	N	18.76
calc %	: C	40.22	H	5.33	N	18.50

^{1}H N.M.R., Acetone-D6;

pyrazole resonances, 7.95, dd, H_5 ($^3J_{4,5}$=2.49, $^4J_{3,5}$=0.72 Hz), 1H; 7.60, dd, H_3($^3J_{3,4}$=2.10, $^4J_{3,5}$=0.80 Hz), 1H; 6.32, dd, H_4($^3J_{4,5}$=2.52, $^3J_{3,4}$=2.10 Hz),1H.

N-methylimidazole resonances, 7.11, d, $H_{4(5)}$ ($^3J_{4,5}$=1.35 Hz), 1H; 6.96, d, $H_{5(4)}$ ($^3J_{4,5}$=1.35 Hz), 1H; 3.9, s, N**Me**, 3H.

5.57, s, CH_2, 2H; 0.09, s, Pd**Me** *trans* to pz, 3H; -0.01, s, Pd**Me** *trans* to mim, 3H.

Spectra remain unchanged to -70°C.

(xv) 1,10-Phenanthroline, phen,

{$PdMe_2$(phen)} prepared in acetone in 74% yield; m.pt. 195°C (decomp.).

Analysis;

found %	: C	53.05	H	4.42	N	9.20
calc %	: C	53.10	H	4.46	N	8.85

^{1}H N.M.R., Acetone-D6;

9.12, dd, $H_{2,9}$ ($^3J_{2,3}$=4.86, $^4J_{2,4}$=1.52 Hz), 2H; 8.76, dd, $H_{4,7}$ ($^3J_{3,4}$=8.18, $^4J_{2,4}$=1.52 Hz), 2H; 8.17, s, $H_{5,6}$, 2H; 8.04, dd, $H_{3,8}$ ($^3J_{2,3}$=4.87, $^3J_{3,4}$=8.21 Hz), 2H; 0.38, s, Pd**Me**, 6H.

(xvi) N-Methyl-2-(pyridin-2-yl)imidazole, pymim,

{$PdMe_2$(pymim)} prepared in acetone in 69% yield; m.pt. 140°C (decomp.).

Analysis;

found %	: C	44.37	H	5.02	N	13.99
calc%	: C	44.69	H	5.11	N	14.21

^{1}H N.M.R., Acetone-D6;

pyridine resonances, 8.68, d, H_6 ($^3J_{5,6}$=5.02 Hz), 1H; 8.10, m, $H_{3,4}$, 2H; 7.56, ddd, H_5 ($^3J_{5,6}$=5.16, $^3J_{4,5}$=7.10, $^4J_{3,5}$=1.81 Hz), 1H.

N-methylimidazole resonances, 7.42, s, $H_{4(5)}$, 1H; 7.12, s, $H_{5(4)}$, 1H; 4.22, s, N**Me**, 3H.

0.24, s, Pd**Me** *trans* to py, 3H; 0.05, s, Pd**Me** *trans* to mim, 3H.

(xvii) Triphenylphosphine, PPh_3.[13]

$\{PdMe_2(PPh_3)_2\}$ prepared in acetone in 55% yield.

^{1}H N.M.R., Chloroform-D;

7.22, m, PPh_3, 30H; 0.20, m, *cis* Pd**Me**, 6H.

(xviii) {(Pyridin-2-yl)bis(N-methylimidazol-2-yl)}methane, $pymim_2CH$.

$\{PdMe_2(pymim_2CH)\}$ prepared in acetone in 75% yield;

m.pt. 190°C (decomp.).

Analysis;

found %	: C	49.37	H	5.51	N	17.98
calc. %	: C	49.30	H	5.43	N	17.97

^{1}H N.M.R., Acetone-D6;

high, 45°C : *pyridine resonances*, 8.52, ddd, H_6 ($^3J_{5,6}$=4.88, $^4J_{4,6}$=1.81, $^5J_{3,6}$=0.94 Hz), 1H; 8.39, m, H_3 ($^3J_{3,4}$~7.8 Hz), 1H; 7.73, ddd, H_4 ($^3J_{3,4}$~$^3J_{4,5}$~7.6, $^4J_{4.6}$=1.86 Hz), 1H; 7.27, ddd, H_5 ($^3J_{5,6}$=4.89, $^3J_{4,5}$=7.56, $^4J_{3,5}$=1.14 Hz), 1H.

N-methylimidazole resonances, 7.09, d, $H_{4(5)}$ ($^3J_{4,5}$=1.39 Hz), 2H; 7.06, d, $H_{5(4)}$ ($^3J_{4,5}$=1.42 Hz), 2H; 3.91, s, N**Me**, 6H.

0.03, s, Pd**Me**, 6H.

Ambient : all resonances as above with addition of; 6.02, s, CH, 1H;

Spectra remain unchanged to -30°C.

(xix) {N-Methylimidazol-2-yl)bis(pyridin-2-yl)}methane, $mimpy_2CH$.

$PdMe_2(mimpy_2CH)\}$ prepared in benzene in 68% yield; m.pt. 175°C (decomp.).

Analysis;

found %	: C	52.67	H	5.25	N	14.40
calc %	: C	52.79	H	5.21	N	14.49

^{1}H N.M.R., Acetone-D6;

Ambient : *pyridine resonances*, 8.64, d, H6 ($^3J_{5,6}$=4.70 Hz), 2H; 7.96, d, H_3 ($^3J_{3,4}$=7.77 Hz), 2H; 7.81, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.66, $^4J_{4,6}$=1.60 Hz), 2H; 7.30, m, H_5, 2H.

N-methylimidazole resonances, 7.16, d, $H_{4(5)}$ ($^3J_{4,5}$=1.24 Hz), 1H; 6.99, d, $H_{5(4)}$ ($^3J_{4,5}$=1.29 Hz), 1H; 3.99, s, N**Me**, 3H.

6.09, s, C**H**, 1H; 0.02, s, Pd**Me** *trans* to py, 3H; -0.24, s, Pd**Me** *t trans* to mim, 3H.

low, -70°C : *free pyridine resonances*, 8.49, d, H_6 ($^3J_{5,6}$=4.43 Hz), 1H; 7.26, H_5 (obs.), 1H; 7.54, *pseudo* t, H_4 ($^3J_{3,4}$~$^3J_{4,5}$~7.6 Hz), 1H; 7.84, m, H_3, 1H.

bound pyridine resonances, 8.77, d, H_6 ($^3J_{5,6}$=4.62 Hz), 1H; 7.52, m, H_5, 1H; 8.03, m, H_4, 1H; 7.93, d, H_3 ($^3J_{3,4}$~7.5 Hz),1H.

bound N-methylimidazole resonances, 7.30, d, $H_{4(5)}$ ($^3J_{4,5}$~1.25 Hz), 1H; 6.98, d, $H_{5(4)}$ ($^3J_{4,5}$=1.36 Hz), 1H; 4.02, s, N**Me**, 3H.

6.19, s, C**H**, 1H; -0.04 (-0.03 sh), s, Pd**Me** *trans* to py, 3H; -0.16 (-0.15 sh), s, Pd**Me** *trans* to mim, 3H.

(xx) (Pyridin-2-yl)bis(pyrazol-1-yl)}methane, $pypz_2CH$.

{$PdMe_2(pypz_2CH)$} prepared in benzene in 62% yield; m.pt. 130°C (decomp.).

Analysis;

found %	: C	46.04	H	4.69	N	19.12
calc. %	: C	46.49	H	4.74	N	19.36

^{1}H N.M.R., Acetone-D6;

Ambient : all resonances are broad and definitive assignments within each ring system is not possible.

pyridine resonances, 8.66, 8.43, 7.95, 7.50

pyrazole resonances, 8.43, 7.71, 6.47

8.17, s, C**H**, 1H; -0.03, s, Pd**Me**, 6H.

low, -80°C : ***isomer A,*** *free pyridine,* 8.48, d, H_6 ($^3J_{5,6}$~4.4 Hz), 1H; 7.85, ddd, H_4 ($^3J_{3,4}$~$^3J_{4,5}$~7.7, $^4J_{4,5}$=1.46 Hz), 1H; 7.40, m, H_5, 1H; ~6.55, m, H_3, 1H.

bound pyrazole, 8.40, d, H_5 ($^3J_{4,5}$=2.43 Hz), 2H; 7.79, d, H_3 ($^3J_{3,4}$=1.67 Hz), 2H; 6.60, *pseudo* t, H_4 ($^3J_{4(3,5)}$=2.24 Hz), 2H.

8.36, s, CH, 1H; -0.16, s, PdMe, 6H.

isomer B; *free pyrazole,* 9.20, m, H_5 1H; 7.62, d, H_3 ($^3J_{3,4}$=1.57 Hz), 1H, 6.38, *pseudo* t, H_4 ($^3J_{4,(3,5)}$=2.18 Hz), 1H.

bound pyrazole, 8.40, H_5 (obs.), 1H, 7.79, H_3 (obs.), 1H; ~6.56, H_4 (obs.), 1H.

bound pyridine, 8.90, d, H_6 ($^3J_{5,6}$=4.17 Hz), 1H; 8.23, ddd, H_4 ($^3J_{3,4}$~$^3J_{4,5}$~7.8, $^4J_{4,6}$=1.60 Hz), 1H; 8.05, d, H_3 ($^3J_{3,4}$=7.54 Hz), 1H; 7.80, H_5 (obs.), 1H.

8.36, s, CH, 1H; 0.08, s, PdMe, 3H; 0.04, s, PdMe, 3H.

Isomer A and B in *ca.* 5:2 ratio.

(xxi){N-Methylimidazol-2-yl)bis(pyrazol-1-yl)methane, mimpz$_2$CH,

{$PdMe_2$(mimpz$_2$CH)} prepared in benzene in 63% yield; m.pt. 150°C (decomp.).

Analysis;

found %	: C	43.10	H	5.00	N	22.82
calc. %	: C	42.81	H	4.97	N	23.04

^{1}H N.M.R., Acetone-D6;

Ambient : all pyrazole resonances are broad and assignments are not possible.

pyrazole resonances, 9.12, 8.27, 7.77, 7.51, 6.50

N-methylimidazole resonances, 7.33, d, $H_{4(5)}$, ($^3J_{4,5}$=1.36 Hz), 1H; 7.18, d, $H_{5(4)}$ ($^3J_{4,5}$=1.35 Hz), 1H; 3.98, s, NMe, 3H.

0.15, s, PdMe *trans* to pz, 3H; 0.03, s, PdMe,*trans* to mim, 3H.

low, -20°C : *free pyrazole resonances,* 9.19, d, H_5 ($^3J_{4,5}$=2.46 Hz), 1H; 7.54, d, H_3 ($^3J_{3,4}$=1.59 Hz), 1H; 6.35, *pseudo* t, H_4 ($^3J_{4(3,5)}$=2.06 Hz), 1H. *bound pyrazole resonances,* 8.33, d, H_5 ($^3J_{4,5}$=2.61 Hz), 1H; 7.77, d, H_3 ($^3J_{3,4}$=1.84 Hz), 1H; 6.48, *pseudo* t, H_4 ($^3J_{4,(3,5)}$=2.27 Hz), 1H. *bound N-methylimidazole resonances,* 7.38, d, $H_{4(5)}$ ($^3J_{4,5}$=1.35 Hz), 1H; 7.17, d, $H_{5(4)}$ ($^3J_{4,5}$=1.37 Hz), 1H; 3.98, s, NMe, 3H.
0.14, s, PdMe *trans* to pz, 3H; 0.01, s, PdMe *trans* to mim, 3H.

6.4 PREPARATION OF NEUTRAL AND CATIONIC METHYLPALLADIUM(II) COMPLEXES

6.4.1 Preparation of Neutral Complexes

Two methods for the preparation of complexes with the general formula {$PdMeX(L_2)$} (X=I, L_2=bidentate ligand) were developed, and are described below. The first method, in contrast to the second, requires that the ligands used are insensitive to organolithium reagents.

A third method investigated (method C-i and ii) involved oxidative addition of MeI to palladium(0) and palladium(II) substrates.

Method A: From *trans*-{$PdCl_2(SMe_2)_2$} and Methyllithium.

To a cooled (-70°C) suspension of *trans*-{$PdCl_2(SMe_2)_2$} (0.50gm, 1.66mmol) in anhydrous diethyl ether (70cm^3) under a nitrogen atmosphere was added 2 mole equivalents of methyllithium (Li: 0.15gm, MeI: 0.70cm^3). The suspension was stirred for one hour at -60→-40°C to give a near colourless solution with no unreacted starting material evident. Addition of 2,2-bis(pyrazol-1-yl)propane, pz_2CMe_2, (0.29gm, 1.66mmol) with continued stirring while the solution slowly warmed to *ca.* -10°C gave a yellow solution, with little or no reduced palladium present. Hydrolysis, followed by filtration, separation and drying of the organic phase ($MgSO_4$), and evaporation of diethyl ether in a vacuum at *ca.* 5°C, afforded the

crude product {PdMeI(pz_2CMe_2)}. The solid was readily recrystallised from acetone/hexane to give yellow plates {0.51gm, 73%; m.pt. 130°C (decomp.)}.

Analysis;

found %	: C	28.32	H	3.45	N	13.20
calc. %	: C	28.29	H	3.56	N	13.20

^{1}H N.M.R., Acetone-D6;

Ambient : *pz trans to methyl,* 8.14, dd, H_5 ($^3J_{4,5}$=2.73, $^4J_{3,5}$=0.64 Hz), 1H; 8.11, dd, H_3 ($^3J_{3,4}$=2.08, $^4J_{3,5}$=0.54 Hz), 1H; 6.37, dd, H_4 ($^3J_{3,4}$=2.13, $^3J_{4,5}$=2.69 Hz), 1H.

pz trans to iodide, 8.30, dd, H_5 ($^3J_{4,5}$=2.80, $^4J_{3,5}$=0.65 Hz)1H; 7.81, dd, H_3 ($^3J_{3,4}$=2.29, $^4J_{3,5}$=0.67 Hz), 1H; 6.55, dd, H_4 ($^3J_{3,4}$=2.36, $^3J_{4,5}$=2.78 Hz), 1H. 2.83, s, **CMe**, 6H.

0.83, s, Pd**Me**, 3H.

low, -20°C : pyrazole and methylpalladium resonances are similar to those above; 2.95, s, **CMe** (ax), 3H; 2.70, s, **CMe** (eq), 3H;

coalescence temperature=-8°C.

A procedure identical to that described above was employed for the following ligands;

(i) Bis(pyrazol-1-yl)methane, pz_2CH_2,

{PdMeI(pz_2CH_2)} formed in 51% yield; m.pt. 155°C (decomp).

Analysis;

found %	: C	24.17	H	2.60	N	14.11
calc. %	: C	24.23	H	2.80	N	14.13

^{1}H N.M.R.., Acetone-D6;

Ambient : *pz trans to methyl,* 8.03, d, H_5 ($^3J_{4,5}$=2.60 Hz),1H; 7.98, d, H_3 ($^3J_{3,4}$=2.07 Hz), 1H; 6.38, *pseudo* t, H_4 ($^3J_{4,(3,5)}$=2.25 Hz).

pz trans to iodide, 8.21, d, H_5 ($^3J_{4,5}$=2.68 Hz),1H; 7.82, d, H_3 ($^3J_{3,4}$=2.27 Hz), 1H; 6.57, *pseudo* t, H_4 ($^3J_{4,(3,5)}$=2.40 Hz), 1H. 6.85, s, CH_2, 2H; 0.83, s, PdMe, 3H.

low, -30°C : pyrazole and methylpalladium resonances are similar to those above; 7.01, d, CH (eq) (^2J=14.37 Hz), 1H; 6.73, d, CH (ax) (^2J=14.36 Hz), 1H.

(ii) 1,1-Bis(pyrazol-1-yl)ethane, pz_2CHMe,

{PdMeI(pz_2CHMe)} formed in 69% yield; m.pt. 140°C (decomp.).

Analysis;

found %	: C	26.12	H	2.95	N	13.88
calc. %	: C	26.33	H	3.19	N	13.65

^{1}H N.M.R., Acetone-D6;

Ambient : 8.21, s b, H_5, 1H; 8.05, s b, $H_{3,5}$, 2H; 7.81, s b, H_3, 1H; 7.28, s, CH, 1H; 6.60, *pseudo* t, H_4 ($^3J_{4,(3,5)}$~2.3 Hz), 1H; 6.38, *pseudo* t, H_4 ($^3J_{4,(3,5)}$~2.3 Hz), 1H; 2.59, d, CMe (^3J~6.5 Hz), 3H; 0.84, s, PdMe, 3H.

low, -15°C : ***isomer A***, *pz trans to methyl*, 8.07, d, H_5 ($^3J_{4,5}$=2.50 Hz), 1H; 8.06, d, H_3 ($^3J_{3,4}$=1.74 Hz), 1H; ~6.40, m, H_4 (obs.), 1H.

pz trans to iodide, 8.23, d, H_5 ($^3J_{4,5}$=2.50 Hz), 1H; 7.88, d, H_3 ($^3J_{3,4}$=1.84 Hz), 1H; ~6.58, m, H_4 (obs.), 1H.

7.37, q, CH (eq) (^3J=6.73 Hz), 1H; 2.62, d, CMe (ax) (^3J=6.75Hz), 3H; 0.82, s, PdMe, 3H.

isomer B, *pz trans to methyl*, 8.17, d, H_5 ($^3J_{4,5}$=2.51 Hz), 1H; 7.90, d, H_3 ($^3J_{3,4}$=2.25 Hz), 1H; ~6.41, m, H_4 (obs.), 1H.

pz trans to iodide, 8.32, d, H_5 ($^3J_{4,5}$=2.70 Hz),1H; 7.81, d, H_3 ($^3J_{3,4}$=1.90 Hz), 1H; ~6.60, m, H_4 (obs.), 1H.

7.16, q, CH (ax) (^3J=6.80 Hz), 1H; 2.53, d, CMe (eq) (^3J=2.82 Hz), 3H; 0.79, s, PdMe, 3H.

Isomer A and B in *ca.* 8:5 ratio.

(iii) Tris(pyrazol-1-yl)methane, pz_3CH,

{$PdMeI(pz_3CH)$} prepared in 46% yield; m.pt. 135°C (decomp.).

Analysis;

found % : C 29.06 ...H 2.99 N 17.82

calc. % : C 28.56 ...H 2.83 N 18.17

^{1}H N.M.R., Acetone-D6;

Ambient : 9.18, s, CH, 1H; 8.28, s b, $H_{3(5)}$, 3H; 7.98, s b, $H_{5(3)}$, 3H; 6.60 *pseudo* t, H_4 ($^3J_{4,(3,5)}$=2.20 Hz), 3H; 0.73, s, Pd**Me**, 3H.

low, -90°C : *pz trans to methyl*, 8.54, d, H_5 ($^3J_{4,5}$=2.44 Hz), 1H; 8.28, d, H_3 ($^3J_{3,4}$=1.62 Hz), 1H, 6.71, *pseudo* t, H_4 ($^3J_{4,(3,5)}$=2.16 Hz), 1H.

pz trans to iodide, 8.69, s, H_5, 1H; 8.08, s, H_3, 1H; 6.82, s, H_4 1H.

free pz, 7.70, s, H_5, 1H; 7.63, s, H_3, 1H; 6.50, s, H_4 1H.

9.26, s, CH, 1H; 0.62, s, Pd**Me**, 3H.

(iv) 1,2-Di(methylthio)ethane, $MeSCH_2CH_2SMe$,

{$PdMeI(MeSCH_2CH_2SMe)$} prepared in 69% yield; m.pt.125°C (decomp.).

Analysis;

found % : C 16.59 H 3.52

calc. % : C 16.20 H 3.54

^{1}H N.M.R., Acetone-D6;

3.10, m, SCH_2, 4H; 2.41, 2.51, s, S**Me**, 6H; 0.83, s, Pd**Me**, 3H.

Method B: From *trans*-{$PdMe(\mu\text{-}I)(SMe_2)\}_2$ with Addition of Ligands.

To a stirred suspension of *trans*-{$PdCl_2(SMe_2)_2$} (0.30gm, 0.48mmol) in acetone (20cm^3) was added an acetone solution (10cm^3) of 1,1,1-tris(pyrazol-1-yl)ethane, pz_3CMe, (0.22gm, 0.96mmol). The suspension quickly cleared to give a clear, yellow solution free from suspended solids. Filtration, followed by addition of hexane (20cm^3), and slow removal of acetone in a vacuum at ambient temperature afforded the desired complex {$PdMeI(pz_3CMe)$} as a yellow powder, {0.21gm, 45%; m.pt. 120°C (decomp.)}, which did not require recrystallisation.

Analysis;

found % : C 30.48 H 3.21 N 17.31

calc. % : C 30.24 H 3.17 N 17.63

^{1}H N.M.R., Acetone-D6;

Ambient : 8.5-8.0, s, $H_{3,5}$, 6H; 6.56, s, H_4, 3H; 3.04 , s, **CMe**, 3H; 0.54, s, **PdMe**, 3H.

low, -70°C : *free pyrazole*, 7.66, d, H_3 ($^3J_{3,4}$=1.2 Hz), 1H; 6.92, d, H_5 ($^3J_{4,5}$=2.43 Hz), 1H; 6.42, *pseudo* t, H_4 ($^3J_{4,(3,5)}$=2.31 Hz), 1H. *pz trans to methyl*, 8.74, d, H_5 ($^3J_{4,5}$=2.70Hz), 1H; 8.16, d, H_3 ($^3J_{3,4}$=1.86 Hz), 1H; 6.70, *pseudo* t, H_4 ($^3J_{4,(3,5)}$=2.55 Hz), 1H; *pz trans to iodide*, 8.86, d, H_5 ($^3J_{4,5}$=2.82 Hz),1H; 8.00, d, H_3 ($^3J_{3,4}$=1.95 Hz), 1H; 6.82 *pseudo* t, H ($^3J_{4,(3,5)}$=2.55 Hz), 1H. 3.02, s, **CMe**, 3H; 0.44, s, **PdMe**, 3H.

A procedure similar to that described above using either acetone or benzene solvent, as indicated, was employed for the preparation of methyliodopalladium(II) complexes with the following ligands:

(i) Tetrakis(pyrazol-1-yl)methane, pz_4C,

{PdMeI(pz_4C)} prepared in benzene in 49% yield; m.pt. 155°C (decomp.).

Analysis;

found % : C 31.90 H 2.88 N 21.15

calc. % : C 31.81 H 2.86 N 21.20

^{1}H N.M.R., Acetone-D6;

Ambient : All aromatic resonances are broad, and definitive assignments for pyrazole protons is not possible; 8.44, s, 1H; 8.06, s, 1H; 8.00, s, 2H; 7.43, s, 1H; 7.36, s (obs.), 1H; 6.87, s, 2H; 6.52, s, 1H; 6.68, s, 2H, 6.60, s b, 1H; 0.60, s, **PdMe**, 3H.

low, -80°C : ***isomer A,*** *ring a,* 8.40, d, H_3 ($^3J_{3,4}$=1.89 Hz), 1H; ~7.41, m, H_5 (obs.), 1H; ~6.74, m, H_4 (obs.) 1H.

ring b, 8.22, m, H_3 (obs.), 1H; ~6.72, m, H_4 (obs.), 1H; 6.67,d, H_5 ($^3J_{4,5}$=2.73 Hz), 1H.

ring c, 8.10, d, H_3 ($^3J_{3,4}$=1.86 Hz), 1H; 7.58, d, H_5 ($^3J_{4,5}$=3.03 Hz), 1H; ~6.72, m, H_4 (obs.), 1H.

ring d, 8.94, s, H_3, 1H; 6.97, d, H_5 ($^3J_{4,5}$=2.70 Hz), 1H; ~6.72, m, H_4 (obs.), 1H.

0.52, s, Pd**Me**, 3H.

isomer B, *ring e,* 8.30, d, H_3 ($^3J_{3,4}$=1.77 Hz), 1H; 7.54, d, H_5 ($^3J_{4,5}$=2.88 Hz), 1H; 6.57, *pseudo* t, H_4 ($^3J_{4(3,5)}$=2.16 Hz), 1H.

ring f, 8.26, d, H_3 ($^3J_{3,4}$=1.86 Hz), 1H; ~7.40, m, H_5 (obs.), 1H; 6.88, *pseudo* t, H_4 ($^3J_{4,(3,5)}$=2.31 Hz), 1H.

ring g, 8.22, m, H_3 (obs.), 1H; ~6.71, m, H_4 (obs.), 1H; 6.60, d, H_5 ($^3J_{4,5}$=2.73 Hz), 1H.

ring h, 7.90, s, H_3, 1H; 7.31, d, H_5 ($^3J_{4,5}$=2.64 Hz), 1H; ~6.72, m, H_4 (obs.), 1H.

0.60, s, Pd**Me**, 3H.

Isomer A and B in *ca.* 2:1 ratio.

(ii) Bis(pyridin-2-yl)methane, py_2CH_2,

{$PdMeI(py_2CH_2)$} prepared in benzene in 76% yield; m.pt. 175°C (decomp.).

Analysis;

found %	: C	34.29	H	3.09	N	6.61
calc. %	: C	34.44	H	3.13	N	6.69

^{1}H N.M.R., Acetone-D6;

Ambient : *py trans to methyl,* 9.12, ddd, H_6 ($^3J_{5,6}$=5.40, $^4J_{4,6}$=1.71, $^5J_{3,6}$=0.78 Hz), 1H; 7.90, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.68, $^4J_{4,6}$=1.71 Hz), 1H; 7.66, d, H_3 ($^3J_{3,4}$=7.71 Hz), 1H; 7.35, m, H_5, 1H.

py trans to iodide, 8.61, m, H_6, 1H; 8.05, ddd,H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.71, $^4J_{4,6}$=1.65 Hz), 1H; 7.81, d, H_3 ($^3J_{3,4}$=7.56 Hz), 1H; 7.54,m, H_5 1H.

4.91, s, CH (eq), 1H; 4.61, s, CH (ax), 1H; 0.77, s, PdMe, 3H.

low, 0°C : pyridine and methylpalladium resonances as above;

4.92, d, CH (eq) (^2J=13.65 Hz), 1H; 4.61, d, CH (ax) (^2J=13.58 Hz), 1H;

coalescence temperature=307k.

(iii) 1,1-Bis(pyridin-2-yl)ethane, py_2CHMe,

{PdMeI(py_2CHMe)} prepared in benzene in 71% yield; m.pt. 165°C (decomp.).

Analysis;

found %	: C	36.17	H	3.49	N	6.47
calc. %	: C	36.10	H	3.50	N	6.48

^1H N.M.R., Acetone-D6;

isomer A, 9.31, d, H_6 *trans to methyl* ($^3J_{5,6}$=5.59 Hz), 1H; 8.67, d, H_6 *trans to iodide* ($^3J_{5,6}$~4.5 Hz), 1H; 4.86, q, CH (eq) (^3J=7.25 Hz), 1H; 2.59, d, CMe (ax) (^3J=7.25 Hz), 3H; 0.77, s, PdMe, 3H.

isomer B, 9.08, d, H_6 *trans to methyl* ($^3J_{5,6}$~5.9 Hz), 1H; 8.60, d, H_6 *trans to iodide* ($^3J_{5,6}$~4.5 Hz), 1H; 5.42, q, CH (ax) (^3J=7.12 Hz), 1H; ~2.04, CMe (eq) (obs.); 0.78, s, PdMe, 3H.

isomer A and B, 8.06, 7.88, H_4, 2H; 7.75, 7.65, H_3, 2H; 7.54, 7.35, H_5, 2H. *isomer A and B* in *ca.* 5:4 ratio.

(iv) 2,2-Bis(pyridin-2-yl)propane, py_2CMe_2,

{PdMeI(py_2CMe_2)} prepared in benzene in 62% yield; m.pt.155°C (decomp.).

Analysis;

found %	: C	37.34	H	3.92	N	6.27
calc. %	: C	37.65	H	3.84	N	6.27

^{1}H N.M.R., Acetone-D6;

py trans to methyl, 9.44, m, H_6, 1H; 7.92, m, H_4 (obs.), 1H; 7.76, d, H_3 ($^3J_{3,4}$=8.30 Hz), 1H; 7.32, m, H_5, 1H.

py trans to iodide, 8.74, dd, H_6 ($^3J_{5,6}$=5.69, $^4J_{4,6}$~1.6 Hz), 1H; 8.05, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~8.20, $^4J_{4,6}$=1.83 Hz), 1H; 7.89, m, H_3 (obs.), 1H; 7.51, m, H_5, 1H.

3.01, s, **CMe** (ax), 3H; 2.16, s, **CMe** (eq), 3H; 0.79, s, **PdMe**, 3H

(v) 1,1-Bis(pyridin-2-yl)ethene, $py_2C=CH_2$,

{PdMeI($py_2C=CH_2$)} prepared in acetone in 71% yield; m.pt. 155°C (decomp.).

Analysis;

found %	: C	36.15	H	3.03	N	6.42
calc. %	: C	36.27	H	3.04	N	6.51

^{1}H N.M.R., Acetone-D6;

py trans to methyl, 9.23, ddd, H_6 ($^3J_{5,6}$=5.32, $^4J_{4,6}$=1.61, $^5J_{3,6}$=0.69 Hz), 1H; 8.02, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.73, $^4J_{4,6}$=1.76 Hz), 1H; 7.76, m, H_3, 1H; 7.45, ddd, H_5 ($^3J_{5,6}$=5.35, $^3J_{4,5}$=7.60, $^4J_{3,5}$=1.30 Hz), 1H.

py trans to iodide, 8.67, ddd, H_6 ($^3J_{5,6}$=5.68, $^4J_{4,6}$ 1.53, $^5J_{3,6}$=0.60 Hz), 1H; 8.16, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.81, $^4J_{4,6}$=1.71 Hz), 1H; 7.85, ddd, H_3 ($^3J_{3,4}$=7.88, $^4J_{3,5}$=1.44, $^5J_{3,6}$=0.66 Hz), 1H; 7.64, m, H_5, 1H.

6.16, s, $C=CH_2$, 2H; 0.67, s, **PdMe**, 3H.

(vi) Tris(pyridin-2-yl)methane, py_3CH,

{PdMeI(py_3CH)} prepared in acetone in 62% yield; m.pt. 150°C (decomp.).

Analysis;

found %	: C	41.20	H	3.25	N	8.48
calc. %	: C	41.38	H	3.38	N	8.27

^{1}H N.M.R., Acetone-D6;

Ambient : ~8.78, s , H_6, 3H; 7.94, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.71, $^4J_{4,6}$=1.64 Hz), 3H; ~7.64, d b, H_3 ($^3J_{3,4}$~6.13 Hz), 3H; 7.42, m, H_5, 3H; 6.24, s, CH, 1H; 0.35, s, **PdMe**, 3H.

low, -60°C : *py trans to methyl*, 9.16, m, H_6, 1H; 8.13, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.62, $^4J_{4,6}$=1.60 Hz), 1H; 8.00, d, H_3 ($^3J_{3,4}$=7.52 Hz), 1H; 7.53, m, H_5, (obs.), 1H

py trans to iodide and free py (unresolved), 8.53, d, H_6 ($^3J_{5,6}$=4.15 Hz), 2H; 7.94, *pseudo* t, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.4 Hz), 2H; 7.46, m, H_3, H_5, 4H.

6.41, s, CH; 0.26, s, PdMe, 3H.

(vii) Bis(N-methylimidazol-2-yl)methane, mim_2CH_2.

{PdMeI(mim_2CH_2)} prepared in acetone in 89% yield; m.pt. 195°C (decomp.).

Analysis;

found %	: C	28.24	H	3.55	N	13.13
calc. %	: C	28.29	H	3.56	N	13.20

^{1}H N.M.R., Acetone-D6;

mim trans to methyl, 7.52, d, $H_{4(5)}$ ($^3J_{4,5}$=1.5 Hz), 1H; 7.00, d, $H_{5(4)}$ ($^3J_{4,5}$=1.53 Hz), 1H; 3.83, s, NMe, 3H.

mim trans to iodide, 7.22, d, $H_{4(5)}$ ($^3J_{4,5}$=1.59 Hz), 1H; 6.99, d, $H_{5(4)}$ ($^3J_{4,5}$=1.63 Hz), 1H; 3.93, s, NMe, 3H. 4.31, s, CH_2, 2H; 0.60, s, PdMe, 3H. Spectra remain unchanged to -70°C.

(viii) Bis(N-methylimidazol-2-yl) methanone, mim_2CO.

{PdMeI(mim_2CO)} prepared in acetone in 88% yield; m.pt. > 230°C.

Analysis;

found %	: C	27.90	H	3.04	N	12.87
calc. %	: C	27.40	H	2.99	N	12.70

^{1}H N.M.R., Complex too insoluble to obtain spectra in all common deuterated solvents.

Infrared, Nujol;

Near : 1630 , 1292, 1172, 902, 786, 724, 646, 600 cm^{-1}.

(ix) 1,1-Bis(N-methylimidazol-2-yl)ethane, mim_2CHMe.

{$PdMeI(mim_2CHMe)$} prepared in acetone in 73% yield; m.pt. 190°C (decomp.).

Analysis;

found % : C 30.55 H 4.00 N 12.56

calc. % : C 30.13 H 3.91 N 12.77

^1H N.M.R., Acetone-D6;

mim trans to methyl, 7.49, d, $H_{4(5)}$ ($^3J_{4,5}$=1.41 Hz), 1H; 6.97, d, $H_{5(4)}$ ($^3J_{4,5}$=1.42 Hz), 1H; 3.86, s, N**Me**, 3H.

mim trans to iodide, 7.19, d, $H_{4(5)}$ ($^3J_{4,5}$=1.55 Hz), 1H; 6.99, d, $H_{5(4)}$ ($^3J_{4,.5}$=1.55 Hz), 1H; 3.95, s, N**Me**, 3H.

4.80, q, C**H** (ax) (^3J=6.98 Hz), 1H; 1.82, d, C**Me** (eq) (^3J=7.02 Hz), 3H; 0.62, s, Pd**Me**, 3H.

Spectra remain unchanged to -70°C.

(x) 1,1-Bis(N-methylimidazol-2-yl)ethene, $mim_2C{=}CH_2$.

{$PdMeI(mim_2C{=}CH_2)$} prepared in acetone in 82% yield; m.pt. 180°C (decomp.).

Analysis;

found % : C 30.71 H 3.51 N 12.62

calc. % : C 30.26 H 3.46 N 12.83

^1H N.M.R., Acetone-D6;

mim trans to methyl, 7.56, d, $H_{4(5)}$ ($^3J_{4,5}$=1.47 Hz), 1H; 7.15, d, $H_{5(4)}$ ($^3J_{4,.5}$=1.42 Hz), 1H; 3.93, s, N**Me**, 3H.

mim trans to iodide, 7.37, d, $H_{4(5)}$ ($^3J_{4,5}$=1.58 Hz), 1H; 7.08, d, $H_{5(4)}$ ($^3J_{4,5}$=1.55 Hz), 1H; 4.00, s, N**Me**, 3H.

6.33, m, $C{=}CH_2$, 2H; 0.60, s, Pd**Me**, 3H.

(xi) {(Pyridin-2-yl)(N-methylimidazol-2-yl)}methane, pymimCH$_2$,

{PdMeI(pymimCH$_2$)} prepared in acetone in 76% yield; m.pt. 155°C (decomp.).

Analysis;

found % : C 31.66 H 3.42 N 10.02

calc. % : C 31.34 H 3.35 N 9.97

^{1}H N.M.R., Acetone-D6;

isomer A, *py trans to methyl,* 9.35, ddd, H_6 ($^3J_{5,6}$=5.44, $^4J_{4,6}$=1.80, $^5J_{3,6}$=0.81 Hz), 1H; 7.89, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.68, $^4J_{4,6}$=1.80 Hz), 1H; 7.66, d, H_3 ($^3J_{3,4}$=7.54 Hz), 1H; 7.35, m, H_5,1H.

mim trans to iodide, 7.20, d, $H_{4(5)}$ ($^3J_{4,5}$=1.58 Hz), 1H; 6.96, d, $H_{5(4)}$ ($^3J_{4,5}$=1.62 Hz), 1H; 3.94, s, N**Me**, 3H.

4.50, s, CH_2, 2H; 0.80, s, Pd**Me**, 3H.

isomer B, *py trans to iodide and mim trans to methyl* resonances are broad, of low intensity and are partly obscured, and thus definitive assignments are not possible.

3.86, s, N**Me**, 3H; 0.59, s, Pd**Me**, 3H.

Isomer A and B in *ca.* 16:1 ratio.

(xii) 1,1-{(Pyridin-2-yl)(N-methylimidazol-2-yl)}ethane, pymimCHMe.

{PdMeI(pymimCHMe)} prepared in acetone in 76% yield; m.pt. 140°C (decomp.).

Analysis;

The complex formed as an oil at room temperature, and crystallised on standing at -20°C. Attempts to recrystallise this solid failed, and a correct microanalysis of the original product formed could not be obtained.

found % : C 34.57 H 3.85 N 10.01

calc. % : C 33.09 H 3.70 N 9.65

^{1}H N.M.R., Acetone-D6;

py trans to methyl, 9.46, ddd, H_6 ($^3J_{5,6}$=5.36, $^4J_{4,6}$=1.70, $^5J_{3,6}$=0.65 Hz), 1H; 7.89, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.65=1.69 Hz), 1H; 7.65, m, H_3, 1H; 7.34, ddd, H_5 ($^3J_{4,5}$=7.60, $^3J_{5,6}$=5.45, $^4J_{3,5}$=1.48 Hz), 1H.

mim trans to iodide, 7.21, d, $H_{4(5)}$ ($^3J_{4,5}$=1.59 Hz), 1H; 6.98, d, $H_{5(4)}$ ($^3J_{4,5}$=1.59 Hz), 1H; 3.95, s, **NMe**, 3H.

4.86, q, CH (eq) (^3J=7.11 Hz), 1H; 2.24, d, **CMe** (ax) (^3J=7.10 Hz), 3H; 0.80, s, Pd**Me**, 3H.

Spectra remain unchanged to -70°C.

(xiii) 1,1-{(Pyridin-2-yl)(N-methylimidazol-2-yl)}ethene, pymimC=CH_2.

{PdMeI(pymimC=CH_2)} prepared in acetone in 66% yield; m.pt. 165°C (decomp.).

Analysis;

found %	: C	33.14	H	3.39	N	9.62
calc %	: C	33.24	H	3.26	N	9.69

^{1}H N.M.R., Acetone-D6;

py trans to methyl, 9.45, ddd, H_6 ($^3J_{5,6}$=5.40, $^4J_{4,6}$=1.66, $^5J_{3,6}$=0.71 Hz), 1H; 8.01, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.74, $^4J_{4,6}$=1.76 Hz), 1H; 7.82, m, H_3, 1H; ~7.40, m, H_5 (obs.), 1H.

mim trans to iodide, ~7.40, m, $H_{4(5)}$ (obs.), 1H; 7.10, d, $H_{5(4)}$ ($^3J_{4,5}$=1.56 Hz), 1H; 3.95, s, **NMe**, 3H.

6.42, 6.20, s, C=CH_2, 2H; 0.77, s, Pd**Me**, 3H.

(xiv) {(Pyridin-2-yl)(N-methylimidazol-2-yl)methanone, pymimC0.

{PdMeI(pymimC=0)} prepared in acetone in 68% yield; m.pt. 165°C (decomp.).

Analysis;

found %	: C	30.49	H	2.81	N	9.65
calc. %	: C	30.34	H	2.78	N	9.65

^{1}H N.M.R., Acetone-D6

isomer A, *py trans to methyl,* 9.69, ddd, H_6 ($^3J_{5,6}$=5.31, $^4J_{4,6}$=1.47, $^5J_{3,6}$=0.84 Hz), 1H; ~8.25, m, $H_{3,4}$ (obs.), 2H; 7.73, ddd, H_5 ($^3J_{4,5}$=7.83, $^3J_{5,6}$=5.43, $^4J_{3,5}$=2.40 Hz), 1H.

mim trans to iodide, 7.78, d, $H_{4(5)}$ ($^3J_{4,5}$=1.26 Hz), 1H; 7.38, d, $H_{5(4)}$ ($^3J_{4,5}$=1.29 Hz), 1H; 4.12, s, N**Me**, 3H. 0.82, s, Pd**Me**, 3H.

isomer B, *py trans to iodide and mim trans to methyl* resonances are of low itensity and partially obscured, consequently complete assignments are not possible.

py resonances, ~8.8, 8.4, 7.91, *mim* resonances, ~7.8, 7.6.

0.63, s, Pd**Me**.

Isomer A and B in *ca.* 10:1 ratio.

(xv) {(Pyrazol-1-yl)(N-methylimidazol-2-yl)methane, pzmimCH_2 {PdMeI(pzmimCH_2)} prepared in benzene in 58% yield; m.pt.175°C (decomp.).

Analysis;

found %	: C	26.88	H	3.46	N	13.83
calc. %	: C	26.33	H	3.19	N	13.65

^{1}H N.M.R., Acetone-D6;

isomer A, *pz trans to methyl,* 8.06, dd, H_3 ($^3J_{3,4}$=2.13, $^4J_{3,5}$=0.80 Hz), 1H; 7.95, dd, H_5 ($^3J_{4,5}$=2.45, $^5J_{3,5}$=0.82 Hz), 1H; 6.30, *pseudo* t, H_4 ($^3J_{4,(3,5)}$=2.30 Hz), 1H.

mim trans to iodide, 7.29, d, $H_{4(5)}$ ($^3J_{4,5}$=1.54 Hz), 1H; 7.05, d, $H_{5(4)}$ ($^3J_{4,5}$=1.58 Hz), 1H; 4.00, s, N**Me**, 3H.

5.70, s, C**H**, 2H; 0.76, s, Pd**Me**, 3H.

isomer B, *mim trans to methyl,* 7.33, d, $H_{4(5)}$ ($^3J_{4,5}$=1.32 Hz), 1H; 7.08, d, $H_{5(4)}$ ($^3J_{4,5}$=1.32 Hz), 1H; 3.91, s, N**Me**, 3H.

pz trans to iodide, 8.17, d, H_5 ($^3J_{4,5}$=2.33 Hz),1H; 7.72, d, H_3 ($^3J_{3,4}$=2.16 Hz), 1H; 6.48, m, H_4, 1H.

5.73, s, CH, 2H; 0.66, s, PdMe, 3H.

Isomer A and B in *ca.* 19:5 ratio.

(xvi) {(Pyridin-2-yl)(pyrazol-1-yl)}methane, pypzCH$_2$.

{PdMeI(pypzCH$_2$)} prepared in benzene in 57% yield; m.pt. 140°C (decomp.).

Analysis;

found %	: C	29.61	H	3.01	N	10.17
calc. %	: C	29.47	H	2.97	N	10.31

^{1}H N.M.R., Acetone-D6;

isomer A, py trans to methyl, 9.29, ddd, H_6 ($^3J_{5,6}$=5.37, $^4J_{4,6}$=1.69, $^5J_{3,6}$=0.76 Hz), 1H; 8.00, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.67, $^4J_{4,6}$=1.67 Hz), 1H; ~7.70, m, H_3 (obs.), 1H; 7.50, ddd, H_5 ($^3J_{4,5}$=7.62, $^3J_{5,6}$=5.41, $^4J_{3,5}$=1.36 Hz), 1H.

pz trans to iodide, 8.13, dd, H_5 ($^3J_{4,5}$=2.58, $^4J_{3,5}$=0.63 Hz), 1H; ~7.70, m, H_3 (obs.), 1H; 6.51, *pseudo* t, H_4 ($^3J_{4,(3,5)}$=2.41 Hz), 1H.

5.85, s, CH_2, 2H; 0.87, s, PdMe, 3H.

isomer B, pz trans to methyl, 7.95, d, H_5 ($^3J_{4,5}$=2.42 Hz), 1H; 7.82, d, H_3 ($^3J_{3,4}$=1.73 Hz), 1H; 6.32, *pseudo* t, H_4 ($^3J_{4,(3,5)}$=2.29 Hz), 1H.

py trans to iodide, 8.68, d, H_6 ($^3J_{5,6}$~4.5 Hz), 1H; 8.15, m, H_4 (obs.), 1H; 7.87, d, H_3 ($^3J_{3,4}$~7.1 Hz), 1H; ~7.69, m, H_5 (obs.), 1H.

5.87, s, CH_2, 2H; 0.75, s, PdMe, 3H.

Isomer A and B in *ca.* 4:1 ratio.

(xvii){(Pyridin-2-yl)Bis(pyrazol-1-yl)}methane, pypz$_2$CH

{PdMeI(pypz$_2$CH)} prepared in acetone in 62% yield; m.pt. 150°C (decomp.).

Analysis;

found %	: C	33.04	H	2.99	N	14.61
calc. %	: C	32.97	H	2.98	N	14.79

^{1}H N.M.R. Acetone-D6;

Ambient : *py resonances*, 8.80, s, H_6, 1H; 7.97, m, H_4(obs.), 1H; 7.52, m, H_5, 1H; 7.19, s, H_3, 1H.

pz resonances, 8.39, d, H_5 ($^3J_{4,5}$=2.46 Hz), 2H; 7.94, s, H_3, 2H; 6.57, *pseudo* t, H_4 ($^3J_{4,(3,5)}$=2.28 Hz), 2H.

8.31, s, CH, 1H; 0.59, s, Pd**Me**, 6H.

low, -70°C : ***isomer A***, *pz trans to methyl*, 8.44, d, H_5 ($^3J_{4,5}$=2.36 Hz), 1H; 8.11, d, H_3 ($^3J_{3,4}$=1.79 Hz), 6.63, *pseudo* t, H_4 ($^3J_{4,(3,5)}$=2.28 Hz), 1H.

pz trans to iodide, 8.59, d, H_5 ($^3J_{4,5}$=2.37 Hz), 1H; 7.95, d, H_3 ($^3J_{3,5}$=1.67 Hz), 1H; 6.75, *pseudo* t, H_4 ($^3J_{4,(3,5)}$=2.30 Hz), 1H.

free py, 8.56, d, H_6 ($^3J_{5,6}$=4.40 Hz), 1H; 7.92, m, H_4 (obs.), 1H; 7.49, m, H_5, 1H; 6.57, d, H_3 ($^3J_{3,4}$=7.65 Hz), 1H.

8.46, s, CH, 1H; 0.46, s, Pd**Me**, 3H.

isomer B, *py trans to methyl*, 9.53, d, H_6 ($^3J_{5,6}$=5.07Hz), 1H; 8.31, m, H_4, 1H; ~8.10, m, H_3 (obs.), 1H; 7.83, H_5, m, 1H.

pz resonances are all obscured.

0.63, s, Pd**Me**, 3H.

Isomer A and B in *ca.* 6:1 ratio.

(xviii) {(N-Methylimidazol-2-yl)bis(pyrazol-1-yl)}methane, mimpz$_2$CH.

{PdMeI(mimpz$_2$CH)} prepared in acetone in 72% yield; m.pt. 165°C (decomp.).

Analysis;

found %	: C	31.15	H	3.36	N	17.16
calc. %	: C	30.24	H	3.17	N	17.63

Sample contains acetone solvent molecules, N.M.R. identification ($CHCl_3$), and inclusion of "1/4 Acetone" into calculated values gives:

: C 31.18 H 3.38 N 17.11

^{1}H N.M.R., Acetone-D6;

Ambient : all resonances broad with no structure discernable, definitive assignments are not possible.

8.74, 8.44, 8.37, 7.73, 7.50, 7.23, 6.43, 4.11, 3.98, 0.81, 0.66

low, -50°C : ***isomer A,*** *pz trans to methyl,* 8.42, d, H_5 ($^3J_{4,5}$=2.19 Hz), 1H; 8.25, d, H_3 ($^3J_{3,4}$=1.82 Hz), 1H; 6.53, *pseudo* t H_4 ($^3J_{4,(3,5)}$=2.35 Hz), 1H.

mim trans to iodide, 7.66, d, $H_{4(5)}$ ($^3J_{4,5}$=1.35 Hz), 1H; 7.29, d, $H_{5(4)}$ ($^3J_{4,5}$=1.33 Hz), 1H; 4.11, s, N**Me**, 3H.

free pz, 8.66, d, H_5 ($^3J_{4,5}$=2.40 Hz), 1H; 7.74, s, H_3, 1H; 6.50, *pseudo* t, H_4 ($^3J_{4,(3,5)}$=1.97 Hz), 1H.

8.56, s, CH, 1H; 0.76, s, Pd**Me**, 3H.

isomer B, *mim trans to methyl,* 7.56, d, $H_{4(5)}$ ($^3J_{4,5}$=1.25 Hz), 1H; 7.48, d, $H_{5(4)}$ ($^3J_{4,5}$=1.24 Hz); 1H; 3.98, s, N**Me**, 3H.

pz trans to iodide, H_3, H_5?; 6.67, m, H_4, 1H.

free pz, 8.70, m, H_5, 1H; H_3?; H_4?.

CH?; 0.58, s, Pd**Me**, 3H.

Isomer A and B in *ca.* 6:1 ratio.

(xix) {(N-Methylimidazol-2-yl)bis(Pyridin-2-yl)}methane, mimpy$_2$CH.

{PdMeI(mimpy$_2$CH)} prepared in acetone in 46% yield; m.pt. 220°C (decomp.).

Analysis;

found %	: C	35.64	H	4.05	N	14.56
calc. %	: C	35.92	H	3.62	N	13.96

^{1}H N.M.R., Acetone-D6

Ambient : *py resonances,* 9.02, d b, H_6 ($^3J_{5,6}$=4.81 Hz), 2H; 7.88, ddd, H_4 ($^3J_{5,6}$~$^3J_{3,4}$~7.63, $^4J_{4,6}$=1.66 Hz), 2H; 7.71, d, H_3 ($^3J_{3,4}$=7.88 Hz), 2H; 7.37, m, H_5, 2H.

mim resonances, 7.30, s , $H_{4(5)}$, 1H; 7.01, s, $H_{5(4)}$, 1H; 4.13, s, **NMe**, 3H.

6.26, s, CH, 1H; 0.58, s, Pd**Me**, 3H.

low, -95°C : *py trans to methyl*, 9.43, d, H_6 ($^3J_{5,6}$=4.76 Hz), 1H; 8.16, m, H_4,1H; 8.00, d, H_3 ($^3J_{3,4}$=7.64 Hz), 1H; 7.60, m, H_5, 1H.

mim trans to iodide, 7.48, d, $H_{4(5)}$ ($^3J_{4,5}$~1.1 Hz), 1H; 7.05, d, $H_{5(4)}$ ($^3J_{4,5}$~1.1 Hz), 1H; 4.15, s, N**Me**, 3H.

free py, 8.54, d, H_6 ($^3J_{5,6}$=4.23 Hz), 1H; 7.78, m, H_4, 1H; 7.36, m, H_5, 1H; 7.15, d, H_3 ($^3J_{3,4}$=7.80 Hz), 1H.

6.43, s, CH, 1H; 0.44, s, Pd**Me**, 3H.

(xx) {(Pyridin-2-yl)bis(N-methylimidazol-2-yl)}methane, pymim$_2$CH.

{PdMeI(pymim$_2$CH)} prepared in acetone in 46% yield; m.pt. 220°C (decomp.).

Analysis;

found % : C 35.64 H 4.05 N 14.56

calc. % : C 35.92 H 3.62 N 13.96

^{1}H N.M.R., Acetone-D6;

Ambient : *py resonances*, 8.56, ddd, H_6 ($^3J_{5,6}$=4.86, $^4J_{4,6}$=1.78, $^5J_{3,6}$=0.96 Hz), 1H; 7.99, d, H_3 ($^3J_{3,4}$=7.95 Hz), 1H; 7.84, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.63, $^4J_{4,6}$=1.82 Hz), 1H; 7.34, ddd, H_5 ($^3J_{4,5}$=7.51, $^3J_{5,6}$=4.84, $^4J_{3,5}$=1.10 Hz), 1H.

mim resonances, 7.64, s , 1H; 7.30, s , 1H; 7.10, s, 1H; 7.06, s, 1H; 4.07, s, N**Me**, 3H.

6.14, s, CH; 1H; 0.61, s, Pd**Me**, 3H.

low, -20°C : *mim trans to methyl*, 7.59, d, H_4 ($^3J_{4,5}$=1.47 Hz), 1H; 7.17, d, H_5 ($^3J_{4,5}$=1.43 Hz), 1H; 3.91, s, N**Me**, 3H.

mim trans to iodide, 7.37, d, $H_{4(5)}$ ($^3J_{4,5}$=1.48 Hz), 1H; 7.05, d, $H_{5(4)}$ ($^3J_{4,5}$=1.54 Hz), 1H; 4.08, s, **NMe**, 3H.

free py, 8.58, m, H_6, 1H; ~7.9, m, H_3, H_4 (obs.), 2H; ~7.36, m, H_5, 1H.

6.13, s, **CH**, 1H; 0.57, s, **PdMe**, 3H.

(xxi) 2,2'-Bipyridyl, bipy.

{PdMeI(bipy)} prepared in acetone in 79% yield; m.pt. 213°C (decomp.)

Analysis;

found %	: C	33.39	H	2.65	C	7.16
calc. %	: C	32.66	H	2.74	C	6.93

^{1}H N.M.R., Acetone-D6;

py trans to methyl, 9.53, ddd, H_6 ($^3J_{5,6}$=5.31, $^4J_{4,6}$=1.73, $^5J_{3,6}$=0.84 Hz), 1H; 8.51, m, H_3 ($^3J_{3,4}$=8.12, $^4J_{3,5}$~1Hz), 1H; 8.20, ddd, H_4 ($^3J_{3,4}$=8.12, $^3J_{4,5}$=7.58, $^4J_{4,6}$=1.73 Hz), 1H; 7.70, ddd, H_5 ($^3J_{4,5}$=7.58, $^3J_{5,6}$=5.31, $^4J_{3,5}$=1.20 Hz), 1H.

py trans to iodide, 8.70, m, H_6 ($^3J_{5,6}$=5.56 Hz), 1H; 8.58, m, H_3 ($^3J_{3,4}$=8.08, $^4J_{3,5}$=1.40, $^5J_{3,6}$=0.82 Hz), 1H; 8.34, ddd, H_4 ($^3J_{3,4}$=8.08, $^3J_{4,5}$=7.56, $^4J_{4,6}$=1.60 Hz), 1H; 7.85, ddd, H_5 ($^3J_{4,5}$=7.56, $^3J_{5,6}$=5.56, $^4J_{3,5}$=1.40 Hz), 1H. 0.83, s, **PdMe**, 3H.

(xxii) 1,10-Phenanthroline monohydrate, phen,

{PdMeI(phen)} prepared in acetone in 78% yield; m.pt. > 230°C.

Analysis;

found %	: C	36.51	H	2.62	N	6.56
calc. %	: C	36.44	H	2.59	N	6.54

^{1}H N.M.R., Acetone-D6;

py trans to methyl, 9.77, dd, $H_{2(9)}$ ($^3J_{2,3}$=4.93, $^4J_{2,4}$=1.66 Hz), 1H; 8.81, dd, $H_{4(7)}$ ($^3J_{3,4}$=8.19, $^4J_{2,4}$=1.76 (Hz), 1H; 8.06, dd, $H_{3(8)}$ ($^3J_{3,4}$=8.24, $^3J_{2,3}$=4.90 Hz), 1H.

py trans to iodide, 9.08, dd, $H_{9(2)}$ ($^3J_{8,9}$=5.14, $^4J_{2,9}$~1.2 Hz), 1H; 8.94, dd, $H_{7(4)}$ ($^3J_{7,8}$=8.14, $^4J_{7,9}$=1.36 Hz), 1H; 8.19, dd, $H_{8(3)}$ ($^3J_{7,8}$=8.18, $^3J_{8,9}$=5.18 Hz), 1H. 8.25, s, $H_{5,6}$, 2H; 1.00, s, PdMe, 3H.

(xxiii) N-Methyl-2-(pyridin-2-yl)imidazole, pymim

{PdMeI(pymim)} prepared in acetone in 81% yield; m.pt. 195°C (decomp.).

Analysis;

found %	: C	29.66	H	2.93	N	10.25
calc. %	: C	29.47	H	2.97	N	10.31

^{1}H N.M.R., Acetone-D6;

py trans to methyl, 9.31, ddd, H_6 ($^3J_{5,6}$=5.22, $^4J_{4,6}$=1.74, $^5J_{3,6}$=0.92 Hz), 1H; 8.21, d, H_3 ($^3J_{3,4}$=8.13 Hz), 1H; 8.14, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~8.1, $^4J_{4,6}$=1.74 Hz), 1H; ~7.58, m, H_5 (obs.), 1H.

mim trans to iodide, 7.56, d, $H_{4(5)}$ ($^3J_{4,5}$=1.48 Hz), 1H; 7.21, d, $H_{5(4)}$ ($^3J_{4,5}$=1.42 Hz), 1H; 4.31, s, NMe, 3H. 0.91, s, PdMe, 3H.

(xxiv)Triphenylphosphine, PPh_3.

trans-{$PdMeI(PPh_3)_2$} prepared in acetone in 82% yield.

^{1}H N.M.R., Chloroform-D;

7.68, 7.36, m, PPh_3, 30H; 0.23, t, PdMe ($J_{P\text{-}H}$=5.91 Hz), 3H. [Lit.,[14] 0.22, t, PdMe, 3H].

Method C: via Oxidative Addition of MeI.

(i) From MeI and {$Pd_2(dba)_3$ ($CHCl_3$)}

To a cooled (O°C) suspension of {$Pd_2(dba)_3(CHCl_3)$} (0.275g, 0.27 mmol) in benzene (30cm^3) under a nitrogen atmosphere was added, with stirring, iodomethane (0.5 cm^3, 8.03 mmol), followed by 2,2'-bipyridyl (0.09 gm, 0.61 mmol). The mixture was slowly warmed to *ca.* 50°C to yield a yellow solution containing an orange-tan solid. Evaporation to dryness, followed by extraction of the tan solid with diethyl ether (4x10 cm^3), to remove liberated dba, afforded crude {PdMeI(bipy)}. This solid could be readily recrystallised from hot acetone or dichloromethane/hexane

to give pure {PdMeI(bipy)}(0.17 gm, 79%, m.pt. 210°C (decomp)} (N.M.R. verification).

A similar procedure with addition of pz_2CH_2 or py_2CH_2, and recrystallisation from acetone/hexane afforded {PdMeI(pz_2CH_2)} and {PdMeI(py_2CH_2)} in 11% and 38% yield, respectively (N.M.R. identification).

(ii) From MeI and {$PdMe_2(L_2)$}

To a clear colourless solution of {$PdMe_2(pz_2CMe_2)$} (0.30 g, 0.96 mmol) in acetone (20 cm^3) was added iodomethane (0.10 cm^3, 1.6 mmol). Reaction occurred immediately, as evidenced by the evolution of a gas, found to be ethane (g.c./m.s.), and the formation of a pale yellow solution. Filtration, followed by addition of hexane (5 cm^3), and slow evaporation in a vacuum at 10°C afforded {PdMeI(pz_2CMe_2)} as orange crystals (0.28 gm, 68%; m.pt. 159°C (decomp.)} (N.M.R. identification).

An identical procedure to that described above was used for the preparation of a variety of {PdMeI(L_2)} complexes from the corresponding dimethylpalladium(II) complexes and iodomethane, and successful preparations are listed, along with yields obtained, in Table 3.3.2-1.

An analogous procedure to that described above, but with the addition of allyl bromide, was used to prepare the following complexes :

(i) [Pd(η^3-allyl)(pz_2CMe_2)][Pd(η^3-allyl)Br_2], prepared in 63% yield;
m.pt. 140°C (decomp.).

Analysis;

found %	: C	28.81	H	3.51	N	8.86
Calc. %	: C	28.55	H	3.51	N	8.88

^{1}H N.M.R., Acetone-D6;

Ambient : all resonances are broad, and definitive assignments are not possible :
7.89, 7.70, 6.38, 5.58, 4.14, 3.10, 2.40.

low, -65°C : [Pd(η^3-allyl)(pz_2CMe_2)], 8.59, d, H_5 ($^3J_{4,5}$=2.76 Hz), 2H; 8.26, d, H_3 (^3J=1.88 Hz), 8.20, s, H_3, 2H; 6.73, *pseudo* t, H_4 ($^3J_{4,(3,5)}$=2.30 Hz), 6.70, s, H_4, 2H; 6.16, m, $PdCH_2CHCH_2$,1H; 4.68, 4.49, d, CH_{cis} (^3J~6.72 Hz); ~3.81, m (obs.), CH_{trans}, 2H; 2.80, 2.76, 2.42, s, **CMe**, 6H.

[Pd(η^3-allyl)Br_2], 5.06, m, $PdCH_2CHCH_2$, 1H; ~3.81, m (obs.), CH_{cis}, 2H; 2.62, d, CH_{trans} (^3J=12.0 Hz), 2H.

(ib) [Pd(η^3-allyl)(pz_2CMe_2)]BF_4 was prepared by reaction of (i) above with $AgBF_4$ in acetone at ambient temperature. Filtration, to remove precipitated AgBr, followed by addition of hexane and slow removal of acetone afforded the title complex as a white crystalline solid (22%, m.pt. 190°C (decomp.)).

Analysis;

found %	: C	34.98	H	4.14	N	13.41
calc. %	: C	35.11	H	4.17	N	13.65

1H N.M.R., Acetone-D6;

Ambient : 8.43, d, H_5 ($^3J_{4,5}$=2.85 Hz), 2H; 8.10, d, H_3 ($^3J_{4,5}$=1.80 Hz), 2H; 6.63, dd, H_4 ($^3J_{3,4}$=1.75, $^3J_{4,5}$=2.80 Hz), 2H; 8.12, m, $PdCH_2CHCH_2$,1H; 4.56, d, CH_{cis} (^3J=7.0 Hz), 2H; 3.63, d, CH_{trans} (^3J=12.4 Hz), 2H; 2.74, 2.56, s, **CMe**, 6H.

low, -70°C : <u>*isomer A*</u>, 8.26, d, H_3 ($^3J_{3,4}$=2.05), 2H; 6.75, *pseudo* t, H_4 ($^3J_{4,(3,5)}$=2.41 Hz), 4.50, d, CH_{cis} (^3J=6.85 Hz), 2H; 3.60, d, CH_{trans} (^3J=12.50 Hz), 2H; 2.73, 2.42, s, **CMe**, 6H.

<u>*isomer B*</u>, 8.17, d, H_3 ($^3J_{3,4}$=1.99 Hz), 2H; 6.71, *pseudo* t, H_4 ($^3J_{4,(3,5)}$=2.42 Hz), 2H; 4.67, d, CH_{cis} (^3J=6.90 Hz), 2H; 3.66, d, CH_{trans} (^3J=12.52 Hz), 2H; 2.77, 2.75, s, **CMe**, 6H.

<u>*isomer A and B*</u>, 8.56, d, H5 ($^3J_{4,5}$=2.37), 2H; 6.14, m, $PdCH_2CHCH_2$, 1H.

<u>*isomer A and B*</u> in *ca.* 4:3 ratio.

(ii) [Pd(η^3-allyl)(bipy)]Br, prepared in 79% yield; m.pt. 200°C (decomp.).

Analysis;

found %	: C	40.32	H	3.41	N	7.21
calc. %	: C	40.71	H	3.42	N	7.30

^{1}H N.M.R., Complex is too insoluble in all common solvents to obtain a spectrum.

6.4.2 Preparation of Neutral Complexes by Halide Exchange

Complexes with the general formula {PdMeX(L_2)} (X=Cl or Br, L_2=ligand) were prepared by removal of iodide ion from *trans*-{PdMe(μ-I)(Me_2S)}$_2$, followed by addition of Cl^- or Br^-, and ligands. A detailed description of one such complex is given below:

To a stirred acetonitrile solution (50cm^3) of *trans*-{PdMe(μ-I)(SMe_2)}$_2$ (0.30gm, 0.48mmol) was added $AgNO_3$ in acetonitrile (3.6cm^3, 1.15mmol). Filtration to remove precipitated AgI, followed by addition of an aqueous solution of KBr (0.23gm, 1.92mmol), and filtration to remove remaining Ag^+ as AgBr gave a clear, yellow solution. Gentle heating (50°C) for *ca.* 15 minutes followed by addition of bipy (0.15gm, 0.96mmol) and removal of organic solvents in a vacuum at *ca.* 50°C gave an orange powder, which was collected by filtration and dried under high vacuum. Recrystallisation could be effected from acetone/hexane to yield yellow-orange {PdMeBr(bipy)}, {0.26gm, 75%; m.pt 230°C (decomp.).}.

Analysis;

found %	: C	35.71	H	2.96	N	7.69
calc. %	: C	36.95	H	3.10	N	7.84

^{1}H N.M.R., Chloroform-D;

9.39, ddd, H_6 *trans to methyl* ($^3J_{5,6}$=5.34, $^4J_{4,6}$=1.70, $^5J_{3,6}$=0.90 Hz), 1H; 8.70, d, H_6 *trans to iodide* ($^3J_{5,6}$~4.93 Hz), 1H; 8.14-7.95, m, H_3, H_4, 4H; 7.61-7.51, m, H_5, 2H; 1.04, s, Pd**Me**, 3H.

A similar procedure, but with gentle heating preceded by addition of additional aqueous KCl, afforded the chloro-analogues. Using these procedures the following complexes were prepared:

(i) {PdMeCl(bipy)},[15] prepared in 73% yield; m.pt. 225°C (decomp.).

^{1}H N.M.R., Chloroform-D;

9.22, m, H_6 *trans to methyl*, 1H; 8.69, d, H_6 *trans to iodide* ($^3J_{5,6}$=4.96 Hz), 1H; 8.14-7.96, m, H_3, H_4, 4H; 7.55, m, H_5, 2H; 1.05, s, PdMe, 3H.

(ii) {PdMeBr(pz_2CMe_2)}, prepared in 66% yield; m.pt 165°C (decomp.).

Analysis;

found %	: C	31.47	H	3.91	N	14.52
calc. %	: C	31.81	H	4.00	N	14.84

^{1}H N.M.R., Acetone-D6,

Ambient : *pz trans to methyl*, 8.13, dd, H_5 ($^3J_{4,5}$=2.73, $^4J_{3,5}$=0.83 Hz), 1H; 8.00, d, H_3 ($^3J_{3,4}$=2.05 Hz), 1H; 6.39, *pseudo* t, H_4 ($^3J_{4(3,5)}$=2.35 Hz), 1H.

pz trans to bromide, 8.29, dd, H_5 ($^3J_{4,5}$=2.97, $^4J_{3,5}$=0.81 Hz), 1H; 7.80, d, H_3 ($^3J_{3,4}$=2.20 Hz), 1H; 6.54, dd, H_4 ($^3J_{4,5}$=2.96, $^3J_{3,4}$=2.20 Hz),1H. 2.72, s, CMe, 6H; 0.84, s, PdMe, 3H.

low, -30°C : pyrazole and methylpalladium resonances as above; 2.93, s, CMe (ax), 3H; 2.69, s, CMe (eq), 3H; coalescence temperature=-13°C

(iii) {PdMeCl(pz_2CMe_2)}, prepared in 57% yield; m.pt. 145°C (decomp.).

Analysis;

found %	: C	35.99	H	4.48	N	16.48
calc. %	: C	36.06	H	4.54	N	16.82

^{1}H N.M.R., Acetone-D6;

Ambient : *pz trans to methyl*, 8.15, dd, H_5 ($^3J_{4,5}$=2.73, $^4J_{3,5}$=0.81 Hz), 1H; 7.90, m, H_3, 1H; 6.39, dd, H_4 ($^3J_{4,5}$=2.70, $^3J_{3,4}$=2.01 Hz), 1H. *pz trans to chloride*, 8.29, dd, H_5 ($^3J_{4,5}$=3.00, $^4J_{3,5}$=0.84 Hz), 1H; 7.78, m, H_3, 1H; 6.52, dd, H_4 ($^3J_{4,5}$=2.94, $^3J_{3,4}$=2.22 Hz), 1H. 2.79, s, C**Me**, 6H; 0.85, s, Pd**Me**, 4H.

low, -40°C : pyrazole and methylpalladium resonances as above; 2.86, s, C**Me** (ax), 3H; 2.66, s, C**Me** (eq), 3H; coalescence temperature=-30°C

(iv) *trans*-{PdMeBr(PPh_3)$_2$}, prepared in 79% yield.

^{1}H N.M.R., Chloroform-D;

7.70, 7.38, m, P**Ph**$_3$, 30H; 0.08, t, Pd**Me** (J_{P-H}=5.97 Hz), 3H. [Lit.,[13] 0.085, t, Pd**Me**, 3H].

(v) *trans*-{PdMeCl(PPh_3)$_2$} prepared in 75% yield.

^{1}H N.M.R., Chloroform-D;

7.70, 7.37, m, P**Ph**$_3$, 30H; -0.03, t, Pd**Me** (J_{P-H}=5.99 Hz), 3H. [Lit.,[13] ^{1}H N.M.R. values not quoted].

6.4.3 Preparation of Cationic Complexes

The general procedure for preparation of complexes with formula [PdMe(L)(L^1)]X (L=bipy; L^1=γ-pic, CH_3CN or SMe_2; X=BF_4), involves removal of iodide ion from *trans*-{PdMe(μ-I)(SMe_2)}$_2$ in the presence of L^1, followed by addition of L. The complex, [PdMe(terpy)]I, however, formed immediately upon treatment of *trans*-{PdMe(μ-I)(SMe_2)}$_2$ with terpy, (see below).

To a stirred suspension of *trans*-{PdMe(μ-I)(SMe_2)}$_2$ (0.30gm, 0.48mmol) in acetone (40cm^3) was added bipy (0.15gm, 0.96mmol), followed by an acetone solution of $AgBF_4$ (10.6cm^3, 0.97mmol), γ-picoline (γ-pic, ~0.2cm^3), and filtration to remove the precipitate formed. Addition of hexane to the filtrate and removal of

acetone in a vacuum at 0°C afforded [PdMe(bipy)(γ-pic)]BF_4 as yellow crystals. Recrystallisation was accomplished from acetone/hexane {0.28gm, 65%, m.pt. 195°C (decomp.)}.

Analysis;

found %	: C	44.54	H	4.02	N	9.05
calc. %	: C	44.63	H	3.97	N	9.18

^{1}H N.M.R., Acetone-D6;

py trans to methyl, 8.67, m, H_3 (obs.), 1H; 8.33, ddd, H_4 ($^3J_{4,5}$~$^3J_{4,5}$~7.70 Hz, $^4J_{4,6}$=1.74 Hz), 1H; 7.84, ddd, H_6 ($^3J_{5,6}$=5.34, $^4J_{4,6}$=1.74, $^5J_{5,6}$=5.32, $^4J_{3,5}$=1.17 Hz), 1H.

py trans to γ-pic, 8.81, m, H_6 (obs.), 1H; 8.70, m, H_3 (obs.), 1H; 8.42, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.65, $^4J_{4,6}$=1.56 Hz), 1H; 7.88, m, H_5, 1H.

γ-pic resonances, 8.84, m, $H_{2,6}$, 2H; 7.66, m, $H_{3,5}$, 2H; 2.56, s, **Me** (γ-pic), 3H. 0.90, s, Pd**Me**, 3H.

An attempted preparation of [PdMe(bipy)(CH_3CN)]BF_4 following the procedure above, *i.e.* the use of CH_3CN in place of γ-pic, gave [PdMe(bipy)(SMe_2)]BF_4 as fine white needles {63%; m.pt. 145°C (decomp.)}.

Analysis;

found %	: C	36.60	H	3.99	N	6.56
calc. %	: C	36.61	H	4.02	N	6.57

^{1}H N.M.R., Acetone-D6;

Ambient : 8.83, s b, H_6 2H; 8.68, m, H_3, 2H; 8.39, m, H_4, 2H; 7.91, m, H_5, 2H; 2.64, s, S**Me**, 6H; 1.05, s, Pd**Me**, 3H.

low, -20°C : *py trans to methyl*, 8.76, d, H_6 ($^3J_{5,6}$~4.5 Hz), 1H; 8.61, d, H_3 ($^3J_{3,4}$=8.14 Hz), 1H; 8.35, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.87, $^4J_{4,6}$=1.60 Hz), 1H; ~7.91, m, H_5 (obs.), 1H.

py trans to dimethylsulphide, 8.72, d, H_6 ($^3J_{5,6}$=5.07 Hz), 1H; 8.66, d, H_3 ($^3J_{3,4}$=8.10 Hz), 1H; 8.38, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.85, $^4J_{4,6}$=1.47 Hz), 1H, ~7.88, m, H_5 (obs.), 1H.

2.63, s, SMe, 6H; 0.95, s, PdMe, 3H.

The acetonitrile complex, $[PdMe(bipy)(CH_3CN)]BF_4$, was prepared by treatment of an acetone suspension of {PdMeI(bipy)} with $AgBF_4$, in the presence of CH_3CN, in an analogous manner to that for γ-pic above. Recrystallisation was found to be unnecessary, {76%; m.pt. 180°C (decomp.)}.

Analysis;

found %	: C	38.18	H	3.47	N	10.16
calc. %	: C	38.51	H	3.48	N	10.36

^{1}H N.M.R., Acetonitrile-D3;

high, 45°C : 8.66, d, H_6 ($^3J_{5,6}$=5.37 Hz), 2H; 8.38, d, H_3 ($^3J_{3,4}$=8.11 Hz), 2H; 8.27, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.75, $^4J_{4,6}$=1.48 Hz), 2H; 7.75, m, H_5, 2H; 2.02, s, CH_3CN, 3H; 1.11, s, PdMe, 3H.

low, 0°C : *py resonances, environment A*, 8.54, d, H_6 ($^3J_{5,6}$=5.14 Hz), 1H; 8.29, m, H_3 (obs.), 1H; 8.20, m, H_4 (obs.), 1H; 7.70, m, H_5 (obs.), 1H; *environment B*, 8.49, d, H_6 ($^3J_{5,6}$=5.70 Hz), 1H; 8.31, m, H_3 (obs.), 1H; 8.23, m, H_4 (obs.), 1H; 7.70, m, H_5 (obs.), 1H. 2.02, s, CH_3CN, 3H; 0.94, s, PdMe, 3H.

To a filtered acetone solution (40cm^3) of *trans*-$\{PdMe(\mu\text{-}I)(SMe_2)\}_2$ (0.2gm, 0.32mmol) was added 2,2':6',2"-terpyridyl, terpy, (0.15gm, 0.64mmol). The desired complex, {PdMe(terpy)}I, precipitated immediately and was isolated by filtration and dried under high vacuum. The complex did not require recrystallisation {0.26gm, 87%, m.pt. 185°C (decomp.)}

Analysis;

found %	: C	39.54	H	2.95	N	8.56
calc. %	: C	39.90	H	2.93	N	8.73

^{1}H N.M.R., Methanol-D4 / Dimethylsulphoxide-D6;

8.10, m, $H_{6,6"}$, 2H; 7.97, m, $H_{3,3"}$, 2H; 7.94-7.84, m, $H_{3',4',5'}$, 3H; 7.81, ddd, $H_{4,4"}$ ($^3J_{4,5}$~$^3J_{3,4}$~7.98, $^4J_{4,6}$=1.62 Hz), 2H; 7.28, ddd, $H_{5,5"}$ ($^3J_{4,5}$=7.68, $^3J_{5,6}$=5.49, $^4J_{3,5}$=1.38 Hz), 2H; 1.09, s, Pd**Me**, 3H.

6.5 PREPARATION AND SPECTROSCOPIC DETECTION OF NEUTRAL AND CATIONIC $Pd^{IV}RMe_2$ COMPLEXES

6.5.1 Preparation of Isolated Palladium(IV) Complexes.

(A) From $Me_2Pd(II)$ complexes with addition of RX.

To a stirred acetone solution (50cm^3) of {$PdMe_2$(bipy)} (0.40gm, 1.37mmol) at 0°C was added iodomethane (0.5cm^3, 8.03mmol). A clear, slightly yellow solution formed immediately and was evaporated in a vacuum at 0°C until *ca.* half the original volume remained (~15 mins). Addition of cold hexane (0°C, 10cm^3), followed by further evaporation in a vacuum of 0°C resulted in the formation of a white, crystalline solid. The solid was collected by filtration, washed with two portions of cold hexane (0°C, 10cm^3), and dried immediately under high vacuum at ambient temperature. The solid, *fac*-{$PdMe_3I$(bipy)} {0.35gm, 60%; m.pt. 100-110°C, 215°C (decomp.)}, did not require recrystallisation and was stored at -20°C.

Analysis;

found %	: C 36.01	H 4.14	N 6.50	I 29.40
calc. %	: C 35.93	H 3.94	N 6.45	I 29.2

^{1}H N.M.R., Acetone-D6;

8.95, ddd, H_6 ($^3J_{5,6}$=5.27, $^4J_{4,6}$=1.66, $^5J_{3,6}$=0.78 Hz), 2H; 8.65, m, H_3 ($^3J_{3,4}$=8.12, $^4J_{3,5}$~1 Hz), 2H; 8.25, ddd, H_4 ($^3J_{3,4}$=8.12, $^3J_{4,5}$=7.60, $^4J_{4,6}$=1.66 Hz), 2H; 7.80, ddd, H_5 ($^3J_{4,5}$=7.60, $^3J_{5,6}$=5.27, $^4J_{3.5}$=1.17 Hz), 2H; 1.85, s, Pd**Me** (eq), 6H; 1.14, s, Pd**Me** (ax), 3H.

Molecular Weight, $CHCl_3$ 25°C;

found : 447

calc. : 434

While most palladium(IV) complexes reported in this section have been prepared by an analogous method to that outlined above, a more convenient procedure, described below, involves the isolation of palladium(IV) complexes from an *in situ* reaction of $\{PdMe_2(\mu\text{-pyd})\}_n$ (see 6.3), ligands and organohalides.

(B) From $\{PdMe_2(\mu\text{-pyd})\}_n$ with addition of ligands and organohalides.

To a cooled (0°C) acetone suspension (30cm^3) of $\{PdMe_2(\mu\text{-pyd})\}_n$ (0.30gm, 1.39mmol) was added phen (0.25gm, 1.39mmol). The mixture was stirred for 1-2 minutes, then filtered into a precooled (0°C) round-bottomed flask. Addition of iodomethane (0.5cm^3, 8.03mmol), followed by slow evaporation of acetone at 0°C in a vacuum to half the original volume and addition of cold hexane (0°C, 10cm^3), and further evaporation, afforded the desired complex, *fac*-$\{PdMe_3I(phen)\}$. The white solid was collected by filtration, washed with two portions of cold diethyl ether (0°C, 10cm^3), and dried immediately under high vacuum {0.33gm, 52%; m.pt. 100°C, >230°C}.

Analysis;

found %	: C	39.7	H	3.9	N	6.4
calc. %	: C	39.29	H	3.74	N	6.11

^{1}H N.M.R., Acetone-D6;

9.35, dd, $H_{2,9}$ ($^3J_{2,3}$=4.91, $^4J_{2,4}$=1.51 Hz), 2H; 8.91, dd, $H_{4,7}$ ($^3J_{3,4}$=8.21, $^4J_{2,4}$=1.50 Hz), 2H; 8.33, s, $H_{5,6}$ 2H; 8.18, dd, $H_{3,8}$ ($^3J_{3,4}$=8.20, $^3J_{2,3}$=4.88 Hz), 2H; 1.96, s, Pd**Me** *trans to phen*, 6H; 1.20, s, Pd**Me** *trans to iodide*, 3H.

Molecular Weight, $CHCl_3$ 25°C;

found : 479

calc. : 458.

A procedure similar to that described above, using various organohalides (RX), as indicated, was employed for the preparation of Pd(IV) complexes with the following ligands:

(i) N-Methyl-2-(pyridin-2-yl)imidazole, pymim; RX=MeI,

fac-{$PdMe_3I$(pymim)} prepared in 56% yield; m.pt. 120°C, 190°C (decomp).

Analysis; A correct microanalysis of the complex could not be obtained due to reductive elimination of ethane to give {PdMeI(pymim)}.

^{1}H N.M.R., Acetone-D6;

low, 0°C : *py trans to methyl*, 8.86, m, H_6 ($^3J_{5,6}$=5.64 Hz), 1H; 8.31, d, H_3 ($^3J_{3,4}$=8.07 Hz), 1H; 8.20, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.60, $^4J_{4,6}$=1.53 Hz), 1H; 7.68, ddd, H_5 ($^3J_{4,5}$=7.51, $^3J_{5,6}$=5.33, $^4J_{3,5}$=1.16 Hz), 1H. *mim trans to methyl*, 7.55, d, $H_{4(5)}$ ($^3J_{4,5}$=1.18 Hz), 1H; 7.38, d, $H_{5(4)}$ ($^3J_{4,5}$=1.31 Hz), 1H; 4.32, s, NMe, 3H.

1.88, s, PdMe *trans to py*, 3H; 1.65, s, PdMe *trans to mim*, 3H; 1.12, s, PdMe *trans to I*, 3H.

(iia) *Tris*-(pyrazol-1-yl)methane, pz_3CH; RX=MeI,

fac-[$PdMe_3(pz_3CH)$]I prepared in 45% yield; m.pt 110°C (decomp.).

Analysis;

found %	: C 31.86	H 4.2	N 17.42
calc. %	: C 31.70	H 3.89	N 17.06

^{1}H N.M.R., Chloroform-D;

12.02, s, CH, 1H; 8.99, dd, H_5 ($^3J_{4,5}$=2.70, $^4J_{3,5}$=0.7 Hz), 3H; 7.70, d, H_3 ($^3J_{3,4}$~1.8 Hz), 3H; 6.47, dd, H_4 ($^3J_{4,5}$=2.7, $^3J_{3,4}$~2Hz), 3H;1.58, s, PdMe, 9H.

(IIb) Treatment of a cooled (0°C) acetone suspension ($40cm^3$) of (iia) (0.25gm, 0.50mmol) with $AgBF_4$ ($4.2cm^3$, 0.51mmol), followed by filtration, addition of hexane ($20cm^3$), and evaporation of acetone at 0°C in a vacuum afforded $[PdMe_3(pz_3CH)]BF_4$ as white crystals, which were isolated by filtration and dried under high vacuum at ambient temperature. The solid, *fac*-$[PdMe_3(pz_3CH)]BF_4$, {0.15gm, 64% m.pt. 140°C (decomp.)} did not require recrystallisation.

Analysis;

found %	: C	34.34	H	4.22	N	18.31
calc. %	: C	34.50	H	4.23	N	18.57

^{1}H N.M.R., Chloroform-D,

9.60, s, CH, 1H; 8.50, d, H_5 ($^3J_{4,5}$=2.58 Hz), 3H; 7.72, d, H_3 ($^3J_{3,4}$=2.04 Hz), 3H; 6.48, *pseudo* t, H_4 ($^3J_{4,(3,5)}$=2.40 Hz), 3H; 1.58, s, PdMe, 9H.

(iii){(Pyridin-2-yl)bis(pyrazol-1-yl)methane, $pypz_2CH$; RX=MeI,

fac-$[PdMe_3(pypz_2CH)]I$ prepared in 65% yield; m.pt. 115°C (decomp.).

Analysis;

found %	: C	35.88	H	4.02	N	14.0
calc. %	: C	35.56	H	3.98	N	13.82

^{1}H N.M.R., Chloroform-D;

py resonances, 8.87, d, H_3 ($^3J_{3,4}$=7.8 Hz),1H; 8.56, d, H_6 ($^3J_{5,6}$=5.4 Hz), 1H; 8.06, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.8, $^4J_{4,6}$=1.8 Hz), 1H; ~7.6, m, H_5 (obs.), 1H.

pz resonances, 9.01, d, H_5 ($^3J_{4,5}$=2.7 Hz), 2H; ~7.6, m, H_3 (obs.), 2H; 6.43, dd, H_4 ($^3J_{4,5}$=2.6, $^3J_{3,4}$~1.9 Hz), 2H.

10.73, s, CH, 1H; 1.59, s, PdMe *trans to py*, 3H; 1.53, s, PdMe *trans to pz*, 6H.

(iv) {N-Methylimidazol-2-yl)bis(pyrazol-1-yl)} methane, $mimpz_2CH$; RX=MeI,

fac-$[PdMe_3(mimpz_2CH)]I$ prepared in 54% yield; m.pt. 140°C

found %	: C	33.27	H	4.17	N	16.58
calc. %	: C	33.19	H	4.18	N	16.59

^{1}H N.M.R., Chloroform-D;

mim resonances, 7.15, d, $H_{4(5)}$ ($^3J_{4,5}$=1.5 Hz), 1H; 7.00, d, $H_{5(4)}$ ($^3J_{4,5}$=1.5 Hz), 1H; 4.36, s, N**Me**, 3H.

pz resonances, 9.24, dd, H_5 ($^3J_{4,5}$=2.7, $^4J_{3,5}$=0.6 Hz), 2H; 7.62, d, H_3 ($^3J_{3,4}$=1.8 Hz), 2H; 6.39, dd, H_4 ($^3J_{4,5}$=2.7, $^3J_{3,4}$=1.7 Hz), 2H.

10.60, s, C**H**, 1H; 1.56, s, Pd**Me** *trans to pz*, 6H; 1.38, s, Pd**Me** *trans to mim*, 3H.

(v) Tris(pyridin-2-yl)methane, py_3CH; RX=MeI,

fac-[$PdMe_3(py_3CH)$]I prepared in 56% yield; m.pt. 110°C, 170°C (decomp.).

Analysis;

found %	: C	43.02	H	4.31	N	7.83
calc %	: C	43.41	H	4.22	N	7.99

^{1}H N.M.R., Chloroform-D;

8.93, d, H_3 ($^3J_{3,4}$=7.7 Hz), 3H; 8.47, dd, H_6 ($^3J_{5,6}$=5.6, $^4J_{4,6}$=1.7 Hz), 3H; 8.27, s, C**H**, 1H; 7.96, ddd, H_4 ($^3J_{3,4}$~$^3J_{4,5}$~7.7, $^5J_{4,6}$=1.7 Hz), 3H; 7.45, ddd, H_5 ($^3J_{4,5}$=7.7, $^3J_{5,6}$=5.6, $^4J_{3,5}$=1.3 Hz), 3H; 1.50, s, Pd**Me**, 9H.

(vi) {(Pyridin-2-yl)bis(N-methylimidazol-2-yl)}methane, $pymim_2CH$; RX=MeI

fac-[$PdMe_3(pymim_2CH)$]I prepared in 49% yield; m.pt. 135°C (decomp.).

Analysis;

found %	: C	38.57	H	4.54	N	12.97
calc. %	: C	38.40	H	4.55	N	13.17

^{1}H N.M.R., Chloroform-D;

py resonances, 9.38, m, H_3 ($^3J_{3,4}$=7.88 Hz), 1H; 8.50, dd, H_6 ($^3J_{5,6}$=5.24, $^4J_{4,6}$=1.53 Hz), 1H; 7.95, ddd, H_4 ($^3J_{3,4}$~$^3J_{4,5}$~7.67, $^4J_{4,6}$=1.70 Hz), 1H; 7.43, ddd, H_5 ($^3J_{4,5}$=7.61, $^3J_{5,6}$=5.25, $^4J_{3,5}$=1.22 Hz), 1H.

mim resonances, 7.03, d, $H_{4(5)}$ ($^3J_{4,5}$=1.40 Hz), 2H; 6.89, d, $H_{5(4)}$ ($^3J_{4,5}$=1.43 Hz), 2H; 4.32, s, N**Me**, 6H.

7.24, s, C**H**, 1H; 1.55, s, Pd**Me** *trans to py*, 3H; 1.32, s, Pd**Me** *trans to mim*, 6H.

(vii) {(N-Methylimidazol-2-yl)bis(pyridin-2-yl)}methane, mimpy$_2$CH; RX=MeI,

fac-[PdMe$_3$(mimpy$_2$CH)]I prepared in 54% yield; m.pt. 175°C (decomp.).

Analysis;

found %	: C	40.99	H	4.36	N	10.43
calc. %	: C	40.89	H	4.39	N	10.60

^{1}H N.M.R., Chloroform-D;

py resonances, 9.12, m, H$_3$ ($^3J_{3,4}$=7.88 Hz), 2H; 8.47, m, H$_6$ ($^3J_{5,6}$~5.5 Hz), 2H; 7.95, ddd, H$_4$ ($^3J_{4,5}$~$^3J_{3,4}$~7.66, $^4J_{4,6}$=1.67 Hz), 2H; 7.44, ddd, H$_5$ ($^3J_{4,5}$=7.62, $^3J_{4,5}$=7.62, $^3J_{5,6}$=5.30, $^4J_{3,5}$=1.25 Hz), 2H.

mim resonances, 7.03, d, H$_{4(5)}$ ($^3J_{4,5}$=1.47 Hz), 1H; 6.92, d, H$_{5(4)}$ ($^3J_{4,5}$=1.47 Hz), 1H; 4.30, s, N**Me**, 3H.

7.87, s, CH, 1H; 1.53, s, Pd**Me** *trans to py*, 6H; 1.28, s, Pd**Me** *trans to mim*, 3H.

(viii) 2,2'-Bipyridyl, bipy; RX=PhCH$_2$Br,

fac-{Pd(PhCh$_2$)Me$_2$Br(bipy)} prepared in 62% yield; m.pt. 120°C, 175°C (decomp.).

Analysis;

found %	: C	49.45	H	4.56	N	5.97
calc %	: C	49.22	H	4.57	N	6.04

^{1}H N.M.R., Chloroform-D;

bipy trans to methyl, 8.54, m, H$_6$ ($^3J_{5,6}$=5.20 Hz), 2H; 7.98, d, H$_3$ ($^3J_{3,4}$=8.12 Hz), 2H; 7.78, ddd, H$_4$ ($^3J_{4,5}$~$^3J_{3,4}$~7.70, $^4J_{4,6}$=1.61 Hz), 2H; 7.36, ddd, H$_5$ ($^3J_{4,5}$=7.5, $^3J_{5,6}$=5.24, $^4J_{3,5}$=1.08 Hz), 2H.

CH$_2$Ph trans to bromide, 6.73, m, H$_4$, 1H; 6.60, *pseudo* t, H$_3$ (^3J~7.7 Hz), 2H; 6.40, *pseudo* d, H$_2$ (^3J=7.7 Hz), 2H; 3.17, s, PdCH$_2$, 2H.

1.98, s, Pd**Me**, 6H.

(ix) {(Pyridin-2-yl)bis(N-methylimidazol-2-yl)}methane, pymim$_2$CH; RX=EtI (CH_3CH_2I),

fac-[PdEtMe$_2$(pymim$_2$CH)]I prepared in 73% yield; m.pt. 115°C, 230°C (decomp.).

Analysis;

found %	: C	39.60	H	4.71	N	12.70
calc. %	: C	39.62	H	4.80	N	12.83

^{1}H N.M.R., Chloroform-D;

isomer A, *mim trans to methyl*, 7.06, d, $H_{4(5)}$ ($^3J_{4,5}$=1.45 Hz), 2H; 6.88, d, $H_{5(4)}$ ($^3J_{4,5}$=1.44 Hz), 2H; 4.32, s, N**Me**, 6H.

py trans to ethyl, 9.32, d, H_3 ($^3J_{3,4}$=7.80 Hz), 1H; 8.45, dd, H_6 ($^3J_{5,6}$=5.63, $^4J_{4,6}$=1.48 Hz), 1H; 7.91, m, H_4 (obs.), 1H; 7.37, ddd, H_5 ($^3J_{4,5}$=7.60, $^3J_{5,6}$=5.27, $^4J_{3,5}$=1.26 Hz), 1H.

7.13, s, **CH**, 1H; 2.56, q, PdCH_2CH_3 (^3J=7.5 Hz) *trans to py*, 2H; 1.30, s, Pd**Me** *trans to mim*, 6H; 1.09, t, PdCH_2CH_3 (^3J=7.5 Hz), 3H.

isomer B, *mim trans to methyl*, 7.06, m, $H_{4(5)}$ (obs.), 1H; 6.88, m, $H_{5(4)}$ (obs.), 1H; 4.32(5), s, N**Me**, 3H.

py trans to methyl, 9.40, d, H_3 ($^3J_{3,4}$=7.78 Hz), 1H; 8.54, m, H_6 ($^3J_{5,6}$~5.3 Hz), 1H; 7.96, m, H_4 (obs.), 1H; 7.43, m, H_5 (obs.), 1H.

mim trans to ethyl, 6.98, d, $H_{4(5)}$ ($^3J_{4,5}$=1.28 Hz), 1H; 6.84, d, $H_{5(4)}$ ($^3J_{4,5}$=1.22 Hz), 1H; 4.29, s, N**Me**, 3H. 7.20, s, **CH**, 1H; 2.32, m, PdCHHCH$_3$ *trans to mim*, 1H; 2.28, m, PdCHHCH$_3$ *trans to mim*, 1H; 1.55, s, Pd**Me** *trans to py*, 3H; 1.29, s, Pd**Me** *trans to mim*, 3H; 1.02, t, PdCH_2CH_3 *trans to mim*, (^3J=7.57 Hz), 3H.

isomer A and B in *ca.* 5:3 ratio.

(x) {(Pyridin-2-yl)bis(N-methylimidazolyl)}methane, pymim$_2$CH; RX=AllylBr (CH_2=CH-CH_2Br),

fac-[Pd(Allyl)Me$_2$(pymim$_2$CH)]Br prepared in 76% yield; m.pt. 115°C, 190°C (decomp.).

Analysis;

found %	: C	44.43	H	5.03	N	13.58
calc. %	: C	44.68	H	5.13	N	13.71

^{1}H N.M.R., Chloroform-D;

isomer A, *mim trans to methyl,* 7.07, d, $H_{4(5)}$ ($^3J_{4,5}$=1.45 Hz), 2H; 6.88, d, $H_{5(4)}$ (obs.) ($^3J_{4,5}$=1.47 Hz), 2H; 4.37, s, N**Me**, 6H.

py trans to allyl, 9.45, m, H_3 (obs.), 1H; 8.45, dd, H_6 ($^3J_{5,6}$=5.47, $^4J_{4,6}$=1.42 Hz), 1H; ~7.94, m, H_4 (obs.), 1H; ~7.38, m, H_5 (obs.), 1H.

7.53, s, CH, 1H; 3.16, d, $PdCH_2CHCH_2$ *trans to py* (^3J=8.16 Hz), 2H; 1.40, s, Pd**Me** *trans to mim*, 6H.

isomer B, *mim trans to methyl and allyl,* 7.09, d, $H_{4(5)}$ ($^3J_{4,5}$=1.39 Hz), 1H; ~6.88, m, $H_{5(4)}$ (obs.), 1H; 6.99, d, $H_{4(5)}$ ($^3J_{4,5}$=1.41 (Hz), 1H; 6.86, d, $H_{5(4)}$ ($^3J_{4,5}$=1.41 Hz), 1H; 4.38, s, N**Me**, 3H; 4.35, s, N**Me**, 3H.

py trans to methyl, 9.47, m, H_3 (obs.), 1H; 8.55, dd, H_6 ($^3J_{5,6}$=5.14, $^4J_{4,6}$=1.30 Hz), 1H; 7.97, m, H_4 (obs.), 1H; 7.42, m, H_5 (obs.), 1H.

7.59, s, CH, 1H; 2.93, m, $PdCH_2CHCH_2$ *trans to mim*, 2H; 1.62, s, Pd**Me** *trans to py*, 3H; 1.38, s, Pd**Me** *trans to mim,* 3H.

isomer A and B, 5.84, m, $PdCH_2CHCH_2$, 2H; 5.25, m, Pd CH_2CHCHH *trans to* CH, 2H; 5.06, m, $PdCH_2$CHCHH *cis to* CH, 2H.

isomer A and B in *ca.* 6:5 ratio.

(xi) {(Pyridin-2-yl)bis(N-methylimidazol-2-yl)}methane, pymim$_2$CH; RX=PhCH$_2$Br,

fac-[Pd(PhCH$_2$)Me$_2$(pymim$_2$CH)]Br prepared in 58% yield; m.pt. 110°C, 150°C (decomp.).

Analysis;

found %	: C	49.47	H	4.87	N	12.20
calc. %	: C	49.26	H	5.03	N	12.49

^{1}H N.M.R., Chloroform-D;

isomer A, *mim trans to methyl*, 6.71, d, $H_{4(5)}$ ($^3J_{4,5}$=1.43 Hz), 2H; 6.33, d, $H_{5(4)}$ ($^3J_{4,5}$=1.45 Hz), 2H; 4.30, s, NMe, 6H.

py trans to benzyl, 9.34, m, H_3 (obs.), 1H; 8.42, dd, H_6 ($^3J_{5,6}$=5.41, $^4J_{4,6}$=1.31 Hz), 1H; 7.90, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.66, $^4J_{4,6}$=1.64 Hz), 1H; 7.36, m, H_5 (obs.), 1H.

3.67, s, $PdCH_2Ph$, 2H; 1.46, s, PdMe *trans to mim*, 6H.

isomer B, *mim trans to methyl and benzyl*, 6.95, d, $H_{4(5)}$ ($^3J_{4,5}$=1.41 Hz), 1H; 6.83, d, $H_{5(4)}$ ($^3J_{4,5}$=1.44 Hz), 1H; 6.78, d, $H_{4(5)}$ ($^3J_{4.5}$=1.42 Hz), 1H; 6.53, d, $H_{5(4)}$ ($^3J_{4,5}$=1.43 Hz), 1H; 4.36, s, NMe, 3H; 4.27, s, NMe 3H.

py trans to methyl, 9.37, m, H_3 (obs.), 1H; 7.82, ddd, H_4 ($^3J_{4.5}$~$^3J_{3,4}$~7.66, $^4J_{4.6}$=1.73 Hz), 1H; 7.74, dd, H_6 ($^3J_{5,6}$=5.44, $^4J_{4,6}$=1.35 Hz), 1H; 7.09, m, H_5 (obs.), 1H.

3.57, d, PdCHHPh *trans to mim* (^2J=8.38 Hz), 1H; 3.29, d, PdCHHPh *trans to mim* (^2J=8.36 Hz), 1H; 1.66, s, PdMe *trans to py*, 3H; 1.44, s, PdMe *trans to mim*, 3H.

isomer A and B, 7.47, s, CH, 1H; 7.38, s, CH, 1H; 7.2-6.8, m, $PdCH_2Ph$, 10H.

isomer A and B in *ca.* 1:1 ratio.

6.5.2 Preparation of Spectroscopically Detected $Pd^{IV}RMe_2$ Complexes.

During this study numerous Pd(IV) species were generated and detected *in situ* by ^{1}H N.M.R. spectroscopy at low to ambient temperature. Attempts to prepare and isolate these complexes in the laboratory were unsuccessful, due mainly to the ease with which they underwent reductive elimination reactions to form the corresponding monoorganohalopalladium(II) complexes.

The procedure used to generate the Pd(IV) solutions simply involved cooling an acetone, acetonitrile, or chloroform solution of the corresponding $\{PdMe_2(L_2)\}$

complex (L_2=bidentate N-donor ligand) in the variable temperature probe of the spectrometer, an excess of organohalide, dissolved in the same solvent as the complex, was rapidly added and spectra recorded as soon as possible after addition.

Generally, additions were performed in acetone at -50°C, with warming in 5°C increments until oxidative addition commenced and a stable intermediate was produced. Further warming allows the reductive elimination reaction, to form monoorganohalopalladium(II) complexes ({$Pd^{II}RX$}), to be followed. For example, oxidative addition of methyliodide to {$PdMe_2$(bipy)} in acetone at 0°C immediately gives spectra assigned as {$PdMe_3I$(bipy)}. Upon warming to room temperature, ethane is eliminated to give {PdMeI(bipy)}; both ethane and {PdMeI(bipy)} are clearly assignable in the ^{1}H N.M.R. spectrum.

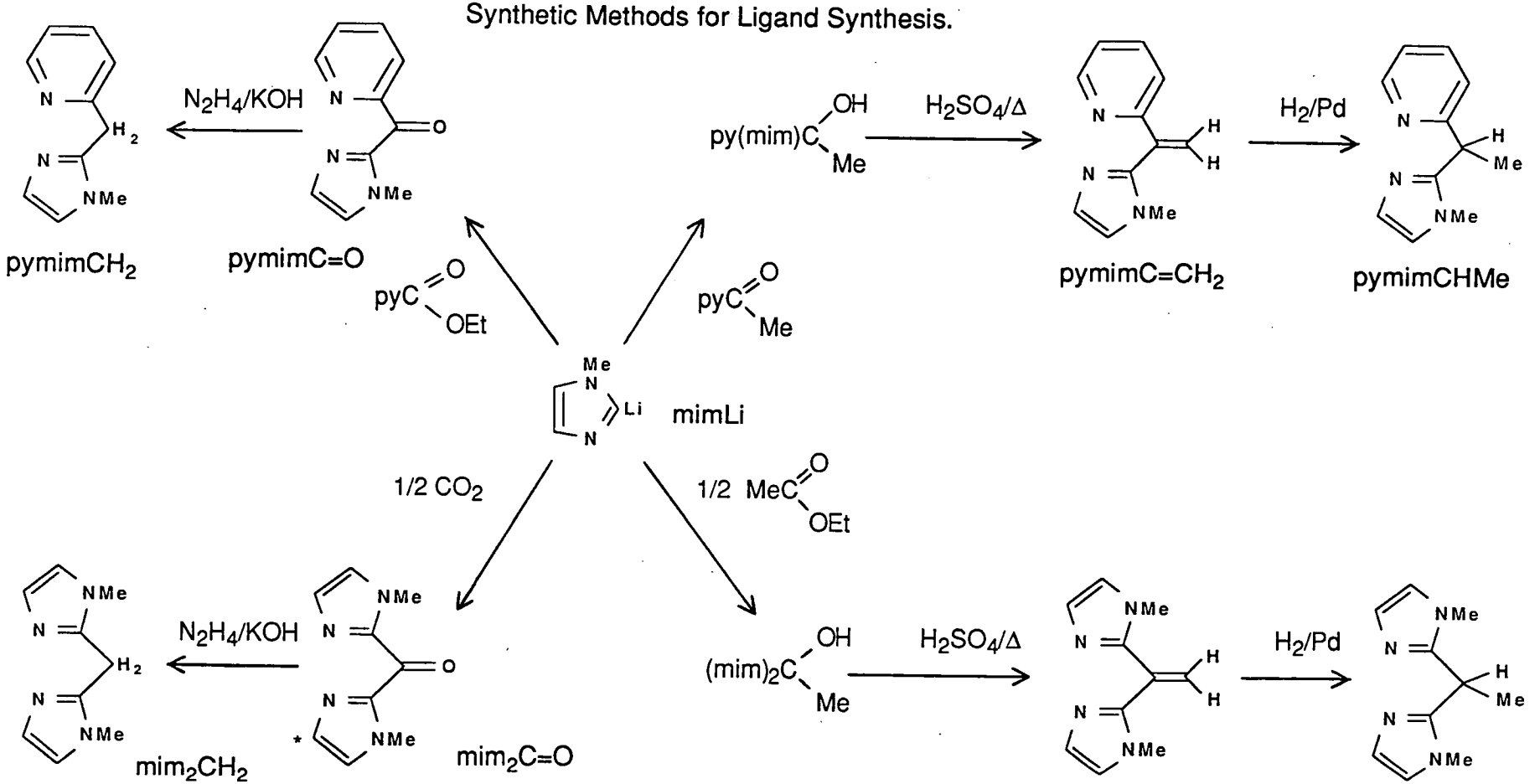
The choice of reaction solvent is difficult to determine *a priori*, but, it was found that acetone solutions allow relatively rapid oxidative addition and reduction elimination reactions, while those for chloroform were considerably slower. Acetonitrile solutions generally behaved in a similar fashion to acetone, but in some instances gave intermediates which were assigned as cations, *i.e.* coordination of CH_3CN molecule in place of I^-.

Tables listing ^{1}H N.M.R. resonance values for *in situ* generated and detected Pd(IV) intermediates can be found in chapter 5.

6.6 PREPARATION OF LIGANDS

For reasons outlined elsewhere a range of new ligands were synthesised during this study. Figure 6.6-1 summarises the synthetic strategy employed for bidentate ligands containing N-methylimidazol-2-yl and pyridin-2-yl rings. Reaction of mimLi with CO_2, pyCOMe, and MeCO(OEt) are new procedures and reaction of mimLi with pyCO(OEt) is an improvement on the reported procedure of Canty *et.al.*[24] Reduction of the ketones with hydrazine is adopted from Newkome's report of the reduction of py_2C=O.

Synthetic Methods for Ligand Synthesis.



* $(mim)_2C{=}O$ has been reported : E. Regel & K.-H. Buchel, J Liebigs Annalen 145 (1977); S.M. Gorun, G. C. Papaefthymiou, R. B. Frankel & S. J. Lippard, JACS **109** 4244 (1987)

The new ligands ligands py_2mimCH and $pymim_2CH$ were obtained directly from $pymimCH_2$ and mim_2CH_2, respectively, on reaction with PhLi and 2-bromopyridine (equations 6.6-1,2), and the two new pyrazol-2-yl containing ligands were obtained according to equations 6.6-3,4.

$$pymimCH_2 + PhLi + Brpy \rightarrow py_2mimCH \qquad 6.6\text{-}1$$

$$mim_2CH_2 + PhLi + Brpy \rightarrow mim_2pyCH \qquad 6.6\text{-}2$$

$$mimCH_2Cl{\cdot}HCl + NH_3 + Kpz \rightarrow mimpzCH_2 \qquad 6.6\text{-}3$$

$$pz_2CO + mimCOH \rightarrow pz_2mimCH \qquad 6.6\text{-}4$$

(i) Bis(Pyrazol-1-yl)methane, pz_2CH_2, was prepared by the method of Julia *et al.*.[16]

^{1}H N.M.R., Acetone-D6

7.85, dd, H_5 ($^3J_{4,5}$=2.40, $^4J_{3,5}$=0.48 Hz), 2H; 7.47, d, H_3 ($^3J_3$=1.78 Hz), 2H; 6.41, s, CH, 2H; 6.27, dd, H_4 ($^3J_{4,5}$=2.37, $^3J_{3,4}$=1.77 Hz), 2H.

(ii) 1,1-Bis(Pyrazol-1-yl)ethane, pz_2CHMe, and

2,2-Bis(Pyrazol-1-yl)propane, pz_2CMe_2, were prepared by the method of The and Peterson,[17] using pz_2CO prepared in the manner described above.

^{1}H N.M.R., Acetone-D6;

pz_2CHMe, 7.80, dd, H5 ($^3J_{4,5}$=2.40, $^4J_{3,5}$=0.45 Hz), 2H; 7.46, s, H_3, 2H; 6.76, q, CHMe (^3J=6.84 Hz), 1H; 6.25, dd, H_4 ($^3J_{4,5}$=2.35, $^3J_{3,4}$=1.83 Hz), 2H; 2.13, d, CHMe (^3J=6.84 Hz), 3H.

pz_2CMe_2, 7.58, dd, H_5 ($^3J_{4,5}$=2.57, $^4J_{3,5}$=0.66 Hz), 2H; 7.47, s, H_3, 2H; 6.24, dd, H_4 ($^3J_{4,5}$=2.40, $^3J_{3,4}$=1.83 Hz), 2H; 2.26, s, CMe, 6H.

(iii) Tris(Pyrazol-1-yl)methane, pz_3CH, was prepared by the method of Canty and Honeyman.[11]

The procedure employed, involved reaction of potassium pyrazolide (KPz) with chloroform (3:1 mole ratio) in tetrahydrofuran. Reflux of the suspension for 8

hours, followed by filtration, and evaporation gave a brown tar. Zone sublimation of this tar gave pyrazole, followed by the desired compound, pz_3CH(~30%).

^{1}H N.M.R., Acetone-D6;

8.74, s, **CH**, 1H; 7.87, d, H_5($^3J_{4,5}$=2.51 Hz), 3H; 7.63, d, H_3 ($^3J_{3,4}$=1.53 Hz), 3H; 6.41, dd. H_4 ($^3J_{4,5}$=2.56, $^3J_{3,4}$=1.75 Hz), 3H.

(iv) 1,1,1-Tris(Pyrazol-1-yl)ethane, pz_3CMe, was prepared by a modification of that given by Canty and Honeyman.[11]

To a chilled (-60°C) solution of pz_3CH (0.75gm, 3.50mmol) in anhydrous diethyl ether (75cm^3) under a nitrogen atmosphere was added commercial Bu^{n}Li (5.8cm^3, 3.55mmol). The thick, white suspension formed was stirred for 5 minutes at -60°C, followed by addition of an excess of MeI (0.75cm^3, 12.0mmol) in anhydrous tetrahydrofuran (30cm^3), and slow warming to room temperature over 2 hours with stirring continued for 2 hours at room temperature. Hydrolysis, and separation of the organic and aqueous phases, followed by extraction of the aqueous phase with chloroform (5x10cm^3), and evaporation of the combined organic phases (predried over $MgSO_4$) gave a yellow oil. Zone sublimation at *ca.* 150°C and 0.1 mmHg, followed by recrystallisation from hot hexane (30cm^3), afforded the desired compound, pz_3CMe, {0.59gm, 74%}.

^{1}H N.M.R., Acetone-D6;

7.67, d, H_3 ($^3J_{3,4}$=1.68 Hz), 3H; 6.94, dd, H_5 ($^3J_{4,5}$=2.69, $^4J_{3.5}$=0.59 Hz), 3H; 6.39, dd, H_4 ($^3J_{4,5}$=2.53, $^3J_{3,4}$=1.76 Hz), 3H; 2.93, s, **CMe**, 3H.

(v) Tetrakis(Pyrazol-1-yl)methane, pz_4C, was prepared by the method of The *et al.*[18]

^{1}H N.M.R., Acetone-D6

7.70, dd, H_3 ($^3J_{3,4}$=1.71, $J_{3,5}$=0.51 Hz), 4H, 7.58, dd, H_5 ($^3J_{4,5}$=2.69, $^4J_{3,5}$=0.61 Hz), 4H; 6.45, dd, H_4 ($^3J_{4,5}$=2.73, $^3J_{3,4}$=1.77 Hz), 4H.

(vi) Bis(Pyridin-2-yl)methane, py_2CH_2, was prepared by the method of Newkome *et al.*[19]

^{1}H N.M.R., Acetone-D6;

8.49, ddd, H_6 ($^3J_{5,6}$=4.85, $^4J_{4,6}$=1.72, $^3J_{3,6}$=0.87 Hz), 2H, 7.68, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.64, $^4J_{4,6}$=1.84 Hz), 2H; 7.32, d, H_3 ($^3J_{3,4}$=7.82 Hz), 2H; 7.19, ddd, H_5 ($^3J_{4,5}$=7.57, $^3J_{5,6}$=4.88, $^4J_{3,5}$=1.15 Hz), 2H; 4.28, s, CH_2, 2H.

(vii) 1,1-Bis(Pyridin-2-yl)ethane, py_2CHMe.[20]

The alkene, $py_2C{=}CH_2$ (preparation given below), was dissolved in ethanol and quantitatively hydrogenated (^{1}H N.M.R. verification) over 3 hours with hydrogen (60 psi) using 5% palladium on charcoal catalyst. On completion the mixture was filtered, evaporated, and the residue distilled at 96-110°C and 0.2 mmHg to yield the desired compound, py_2CHMe, as a clear, slightly yellow oil, {80%}.

^{1}H N.M.R., Acetone-D6;

8.50, d, H_6 ($^3J_{5,6}$=4.63 Hz), 2H; 7.67, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.66, $^4J_{4,6}$=1.86 Hz), 2H; 7.33, d, H_3($^3J_{3,4}$=7.89 Hz), 2H; 7.17, ddd, H_5 ($^3J_{4,5}$=7.45, $^3J_{5,6}$=4.85, $^4J_{3,5}$=1.10 Hz), 2H; 4.46, q, CHMe (^3J=7.21 Hz), 1H; 1.71, d, CHMe (^3J=7.14 Hz), 3H.

(viii) 2,2-Bis(Pyridin-2-yl)propane, py_2CMe_2, was prepared by the method of Canty *et al.*[21]

^{1}H N.M.R., Acetone-D6;

8.49, ddd, H_{67} ($^3J_{5,6}$=4.73, $^4J_{4,6}$=1.84, $^5J_{3,5}$=0.92 Hz), 2H; 7.65, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~8.01, $^4J_{4,6}$=1.91 Hz), 2H; 7.21, d, H_3 ($^3J_{3,4}$=8.03 Hz), 2H; 7.15, ddd, H_5 ($^3J_{4,5}$=7.42, $^3J_{5,6}$=4.85, $^4J_{3,5}$=1.14 Hz), 2H; 1.77, s, CMe, 6H.

(ix) 1,1-Bis(Pyridin-2-yl)ethan-1-ol, py_2CMeOH

To a diethyl ether solution of 2-pyridyllithium (Li : 0.62gm, BrPh : 4.75cm^3; Brpy : 4.3cm^3) at -50°C was slowly added 2-acetylpyridine (5.0cm^3, 45mmol) dissolved in diethyl ether (20cm^3). The thick white suspension formed was allowed to warm slowly to room temperature, followed by a stirring for a further two hours. Water was carefully added to the suspension until both the organic and aqueous phases

were free from salts, and the resulting mixture was allowed to stand overnight. Next day the desired product, py_2CMeOH, had crystallised at the organic/aqueous interface as clear, colourless plates, which were collected by filtration, washed with cold diethyl ether and dried under high vacuum, {4.4gm, 50%, m.pt. 36-38°C}.

Analysis, was not obtained as py_3CMeOH is an intermediate in the preparation of $py_2C{=}CH_2$ and py_2CHMe (see above).

^{1}H N.M.R., Chloroform-D;

8.51, ddd, H_6 ($^3J_{5,6}$=4.86, $^4J_{4,6}$=1.68, $^5J_{3,6}$=0.99 Hz), 2H; 7.76, d, H_3 ($^3J_{3,4}$=8.04 Hz), 2H; 7.64, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.4, $^4J_{4,6}$=1.77 Hz), 2H; 7.14, ddd, H_5 ($^3J_{4,5}$=7.35, $^3J_{5,6}$=4.86, $^4J_{3,5}$=1.20 Hz), 2H; 6.48, s, COH, 1H; 1.98, s, **CMe**, 3H.

Infrared, nujol;

3340(b), 1588, 1572, 1298, 1226, 1156, 1142, 1072, 1046, 994, 802, 756, 618, 590 cm^{-1}.

Mass Spectrum;

m/e (I%) : 200 (M^+, 10%), 199 (20), 185 (40), 183 (35), 122 (100), 104 (20), 78 (30).

(x) 1,1- Bis(Pyridin-2-yl)ethene, $py_2C{=}CH_2$.

A solution of py_2CMeOH (3.5gm, 175mmol) in concentrated sulphuric acid ($100cm^3$) was heated to 160°C for 24 hours. The brown solution was cooled in an ice bath and neutralised **carefully** with a saturated NaOH solution to give precipitated Na_2SO_4, an aqueous phase and the desired crude product as an insoluble oil. The mixture was filtered, and the residue washed with several portions of chloroform. The organic and aqueous phases were separated and the aqueous phase extracted with chloroform ($4x10cm^3$). The combined organic extracts were then passed, with the aid of a vacuum, through a short silica column and evaporated to yield the desired compound, $py_2C{=}CH_2$, as a red oil, {2.55gm, 80%}. Further purification of this oil was not undertaken.

Analysis, was not attempted.

^{1}H N.M.R., Acetone-D6;

8.60, ddd, H_6 ($^3J_{5,6}$=4.70, $^4J_{4,6}$=1.71, $^5J_{3,6}$=0.89 Hz), 2H; 7.78, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.77, $^4J_{4,6}$=1.84 Hz), 2H; 7.43, d, H_3 ($^3J_{3,4}$=7.92 Hz), 2H; 7.32, ddd, H_5 ($^3J_{4,5}$=7.55, $^3J_{5,6}$=4.81, $^4J_{3,5}$=1.11 Hz), 2H; 6.06, s, C=CH_2, 2H.

Infrared, thin film;

1584, 1564, 1472, 1434, 1340, 1152, 1108, 1078, 1048, 992, 926, 800, 760, 664, 630, 606, 576 cm^{-1}.

Mass Spectrum;

m/e (I%) : 182 (M^+, 60%), 181 (100), 169 (20), 104 (20), 78 (20).

(xi) Tris(Pyridin-2-yl)methane, py_3CH, was prepared by the method of Canty *et al.*[21]

^{1}H N.M.R. Acetone-D6;

8.50, ddd, H_6 ($^3J_{5,6}$=4.83, $^4J_{4,6}$=1.77, $^5J_{3,6}$=0.87 Hz), 3H; 7.71, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.74, $^4J_{4,6}$=1.89, Hz), 3H; 7.39, d, H_3 ($^3J_{3,4}$=7.89 Hz), 3H; 7.22, ddd, H_5($^3J_{4,5}$=7.51, $^3J_{5,6}$=4.86, $^4J_{3,5}$=1.11 Hz), 3H; 6.00, s, CH, 1H.

(xii) Bis(N-Methylimidazol-2-yl)methanone, mim_2CO.[22]

To a chilled (-60°C) suspension of mim (15cm^3, 0.19mol) in diethyl ether (150cm^3) under a N_2 atmosphere was slowly added phenyllithium (Li : 2.64gm, BrPh : 20.0cm^3), to give a light tan suspension which upon gradual warming to *ca.* -10°C gave a purple solution. The acetone/CO_2 bath was exchanged for an ice/salt bath, and CO_2 gas, dried by passage through P_2O_5, was passed over the solution surface at a rate of 130 cc/min for 1.5 hours, to give a thick gelatinous suspension; efficient stirring at this stage is essential. Hydrolysis, and careful addition of 4M HCl until the aqueous phase was acidic to blue litmus gave a white emulsion. Passage of the emulsion through filter agent, enabled separation of the organic and aqueous phases. Extraction of the organic phase with 4M HCl (5x10cm^3) and neutralisation of the combined aqueous phases with Na_2CO_3, followed by filtration, and continuous extraction of the filtrate with chloroform for 16 hours gave, upon evaporation of the

chloroform extract, a brown oil. The oil was taken up into chloroform, dried over $MgSO_4$, and passed, with the aid of a vacuum, through a short silica column. Evaporation of chloroform and dissolution of the residue in a minimum volume of dichloromethane, followed by addition of hexane, and slow removal of dichloromethane in a vacuum at ambient temperature afforded the desired compound, mim_2CO, as white crystals which were collected by filtration, washed with hexane and dried under high vacuum, {8.70gm, 48%, m.pt. 145-148°C}.

^{1}H N.M.R., Acetone-D6;

7.38, s, $H_{4(5)}$, 2H; 7.12, s, $H_{5(4)}$, 2H; 3.98, s, **NMe**, 6H.

(xiii) Bis(N-methylimidazol-2-yl)methane, mim_2CH_2, was prepared by an analogous method to that given by Newkome *et al.*[19] for the preparation of py_2CH_2, except in this instance the reaction was performed at 140°C for 4 hours.

Upon cooling, the contents of the bomb were extracted for 12 hours with chloroform. The chloroform extract was dried over $MgSO_4$, filtered, and evaporated to yield a brown solid. Dissolution of the solid in dichloromethane, and passage through a short silica column with the aid of a vacuum, followed by addition of hexane, and slow removal of dichloromethane in a vacuum at ambient temperature gave mim_2CH_2 as cream needles which were collected by filtration, washed with hexane, and dried under high vacuum, {65%, m.pt. 143-148°C}.

Analysis;

found %	: C	61.18	H	6.92	N	31.50
calc. %	: C	61.34	H	6.86	N	31.79

^{1}H N.M.R., Acetone-D6;

6.94, d, $H_{4(5)}$ ($^3J_{4,5}$=1.14 Hz), 2H; 6.77, d, $H_{5(4)}$ ($^3J_{4,5}$=1.11 Hz), 2H; 4.15, s, CH_2, 2H; 3.70, s, **NMe**, 6H.

Infrared, nujol;

1528, 1312, 1288, 1234, 1170, 1146, 1096, 934, 788, 692, 652 cm^{-1}.

Mass Spectrum;

m/e (I%) : 176 (M^+, 100%), 175 (25), 161 (20), 96 (45), 95 (75).

(xiv) 1,1-Bis(N-Methylimidazol-2-yl)ethan-1-ol, mim_2CMeOH.

To a cooled (-60°C) suspension of mim (7.5cm^3, 0.095mol) under a nitrogen atmosphere was added Bu^nLi (95cm^3, 0.095mol). The suspension produced was allowed to warm slowly to *ca.* -10°C before being recooled to -60°C; at this stage a solution virtually free from all solids was obtained. Ethyl acetate (4.6cm^3, 0.047mol) was added in one portion to produce a thick white suspension which was allowed to warm slowly to room temperature, followed by further stirring for two hours. The suspension was carefully hydrolysed with 4M HCl until the aqueous phase was acidic to blue litmus. The organic and aqueous phases were separated, and the organic phase was extracted with 4M HCl (4x10cm^3). The combined aqueous phases were then basified with Na_2CO_3, and continuously extracted for 16 hours with chloroform. The chloroform extract was dried over $MgSO_4$, evaporated, and redissolved in dichloromethane, followed by addition of hexane and slow removal of dichloromethane in a vacuum at ambient temperature, to produce a white, crystalline solid. The solid, mim_2CMeOH, was collected by filtration, washed with diethyl ether and dried under high vacuum, {4.7gm, 48%; m.pt 172-173°C}.

Analysis, was not obtained as mim_2CMeOH is an intermediate in the preparation of $mim_2C{=}CH_2$ and mim_2CHMe.

^1H N.M.R., Chloroform-D;

6.96, d, $H_{4(5)}$ ($^3J_{4,5}$=1.14 Hz), 2H; 6.81, d, $H_{5(4)}$ ($^3J_{4,5}$=1.11 Hz), 2H; 5.51, s br, COH, 1H; 3.28, s, NMe, 6H; 2.05, s, CMe, 3H.

Infrared, nujol;

3108 , 1288, 1240, 1206, 1150, 1120, 1098, 1080, 934, 824, 772 cm^{-1}.

Mass Spectrum;

m/e (I%) : 206 (M^+, 20%), 191 (90), 163 (30), 125 (35), 109 (100), 107 (35), 96 (30), 83 (60).

(xv) 1,1-Bis(N-Methylimidazol-2-yl)ethane, $mim_2C=CH_2$.

An analogous procedure to that employed for the dehydration of py_2CMeOH to $py_2C=CH_2$ (see above) was followed, except for an extended reaction time of 48 hours and elevated reaction temperature of 170°C. After passage through a silica column, a tannish oil was obtained which crystallised on standing [63%, m.pt. 65-70°C].

Analysis, was not attempted.

^{1}H N.M.R., Acetone-D6;

7.09, d, $H_{4(5)}$ ($^3J_{4,5}$=1.01 Hz), 2H; 6.94, d, $H_{5(4)}$ ($^3J_{4,5}$=1.03 Hz), 2H; 5.87, s, $C=CH_2$, 2H; 3.35, s, NMe, 6H.

Infrared, thin film;

1708, 1620, 1524, 1472, 1456, 1410, 1364, 1284, 1078, 1042, 938, 924, 782, 760, 734, 692 cm^{-1}.

Mass Spectrum;

m/e (I%) : 188 (M^+, 100%), 187 (75), 173 (40), 172 (20), 107 (30).

(xvi) 1,1-Bis(N-Methylimidazol-2-yl)ethane, mim_2CHMe.

Hydrogenation of $mim_2C=CH_2$ to yield mim_2CHMe was accomplished by an identical method to that employed for the hydrogenation of $py_2C=CH_2$ to py_2CHMe. After filtration and evaporation of ethanol, the crude product was recrystallised from dichloromethane/hexane to afford mim_2CHMe as white needles, [85%; m.pt. 82-83°C].

Analysis;

found %	: C	62.85	H	7.43	N	28.93
calc. %	: C	63.13	H	7.42	N	29.45

^{1}H N.M.R., Acetone-D6;

6.94, d, $H_{4(5)}$ ($^3J_{4,5}$=1.07 Hz), 2H; 6.80, d, $H_{5(4)}$ ($^3J_{4,5}$=1.11 Hz), 2H; 4.56, q, CHMe (^3J=7.32 Hz), 1H; 3.45, s, NMe, 6H; 1.70, d, CHMe (^3J=7.32 Hz), 3H.

Infrared, nujol;

1500, 1408, 1368, 1280, 1132, 1074, 1042, 772, 744, 700 cm^{-1}.

Mass Spectrum;

m/e (I%) : 190 (M^+, 60%), 189 (30), 175 (45), 109 (40), 107 (35), 96 (100), 95 (50).

(xvii) {(Pyridin-2-yl)(Pyrazol-1-yl)} methane, pypzCH_2, was prepared by the method of Canty and Honeyman.[11]

The procedure involved reaction of 2-(chloromethyl)pyridine with potassium pyrazolide in tetrahydrofuran. Reflux for 3 hours, followed by filtration, and evaporation gave a yellow-red oil. Distillation under high vacuum gave unreacted 2-(chloromethyl)pyridine followed by pypzCH_2 (~90-110°C, 0.2 mmHg).

^{1}H N.M.R., Acetone-D6;

py resonances, 8.54, d, H_6 ($^3J^{5,6}$=4.4Hz), 1H; 7.72, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.74, $^4J_{4,6}$=1.81 Hz), 1H; 7.28, m, H_5 1H; 6.98, d, H_3 ($^3J_{3,4}$=7.75 Hz), 1H.

pz resonances, 7.78, d, H_5 ($^3J_{4,5}$=2.25 Hz), 1H; 7.49, d, H_3 ($^3J_{3,4}$=1.50 Hz), 1H; 6.30, *pseudo* t, H_4 ($^3J_{4(3,5)}$=2.00 Hz), 1H.

5.46, s, CH_2 2H.

(xviii) {(Pyrazol-1-yl)(N-Methylimidazol-2-yl)}methane, pzmimCH_2, was prepared by a modification of the procedure described by Canty and Honeyman.[11]

The modification involved neutralization of the salt, mimCH_2Cl.HCl,[23] immediately prior to reaction with potassium pyrazolide. The procedure required bubbling anhydrous ammonia gas through a suspension of mimCH_2Cl.HCl in anhydrous benzene for 10 minutes. The suspension was purged of excess NH_3 by bubbling N_2 through the suspension for 15 minutes with gentle warming to *ca.* 40°C. Filtration under N_2, through filter agent (celite), gave a clear, colourless solution of mimCH_2Cl, which was reacted with **one** mole equivalent of potassium pyrazolide.

^{1}H N.M.R., Acetone-D6;

pz resonances, 7.59, d, H_5 ($^3J_{4,5}$=2.10 Hz), 1H; 7.42, d, H_3 ($^3J_{3,4}$~1.29 Hz), 1H: 6.24, *pseudo* t, H_4 ($^3J_{4(3,5)}$=2.01 Hz), 1H.

mim resonances, 7.02, d, $H_{4(5)}$ ($^3J_{4,5}$=1.14 Hz), 1H; 6.85, d, $H_{5(4)}$ ($^3J_{4,5}$=1.09 Hz), 1H; 3.72, s, NMe, 3H.

5.40, s, CH_2, 2H.

(xix) N-methyl-2-(Pyridin-2-yl)imidazole, pymim, was prepared by the method of Canty *et al.*[21]

^{1}H N.M.R. Acetone-D6;

py resonances, 8.60, d, H_6 ($^3J_{5,6}$=4.76 Hz), 1H; 8.19, d, H_3 ($^3J_{3,4}$=8.07 Hz), 1H; 7.85, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.7, $^4J_{4,6}$=1.82 Hz)1H; 7.31, ddd, H_5 ($^3J_{4,5}$=7.52, $^3J_{5,6}$=4.87, $^4J_{3,5}$=1.18 Hz).

mim resonances, 7.18, s, $H_{4(5)}$, 1H; 7.02, d, $H_{5(4)}$, 1H; 4.18, s, NMe, 3H.

(xx) {(Pyridin-2-yl)(N-Methylimidazol-2-yl)methanone, pymimCO, was prepared by a modification of the method reported by Canty *et al.*[24]

The modification involved the inverse addition, *via* a jacketed dropping funnel cooled to -50°C, of one mole equivalent of 2-lithio-N-methylimidazole to a cooled (-60°C) diethyl ether solution of ethyl picolinate. The white suspension formed was worked up in an identical manner to that described by Canty *et al.*. Yields of pymimC0 were generally in the range 60-70%.

^{1}H N.M.R., Acetone-D6;

py resonances, 8.70, ddd, H_6 ($^3J_{5,6}$=4.67, $^4J_{4,6}$=1.52, $^5J_{3,6}$=0.94 Hz), 1H; 8.08, m, H_3 ($^3J_{3,4}$=7.84 Hz), 1H; 7.95, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.63, $^4J_{4,6}$=1.76 Hz), 1H; 7.55, ddd, H_5 ($^3J_{4,5}$=7.49, $^3J_{5,6}$=4.67, $^4J_{3,5}$=1.26 Hz), 1H.

mim resonances, 7.48, s, $H_{4(5)}$, 1H; 7.15, s, $H_{5(4)}$, 1H; 4.11, s, NMe, 3H.

(xxi){(Pyridin-2-yl)(N-Methylimidazol-2-yl)methane, pymimCH_2

Reduction of pymimC0 to pymimCH_2 was accomplished by a similar procedure to that employed for the preparation of py_2CH_2 and mim_2CH_2. In this instance, however, the bomb was heated to 140°C for three hours followed by 160°C for 1 hour. Upon cooling, the contents of the bomb were continuously extracted with chloroform for *ca.* 6 hours. The chloroform extract was dried ($MgSO_4$), filtered, and evaporated to yield a brown oil. Distillation of this oil at 100-110°C and 0.22 mmHg

afforded the desired compound, pymimCH_2 {81%, m.pt. *ca.* 20°C}, as a clear, slightly yellow oil.

Analysis, was not attempted.

^{1}H N.M.R., Acetone-D6;

py resonances, 8.47, ddd, H_6 ($^3J_{5,6}$=4.79, $^4J_{4,6}$=1.65, $^5J_{3,6}$=1.05 Hz), 1H; 7.68, ddd, H_4 ($^3J_{4,5}$~^{3}3,4~7.63, $^4J_{4,6}$=1.86 Hz), 1H; ~7.20, m, H_3, H_5, 2H.

mim resonances, 6.97, d, $H_{4(5)}$ ($^3J_{4,5}$=1.17 Hz), 1H; 6.81, d, $H_{5(4)}$ ($^3J_{4,5}$=1.17 Hz), 1H; 3.64, s, NMe, 3H.4.22, s, CH_2, 2H.

Infrared, thin film;

3104, 3004, 2944, 1592, 1572, 1520, 1498, 1476, 1436, 1412, 1282, 1148, 1122, 996, 926, 752, 664 cm^{-1}.

Mass Spectrum;

m/e (I%) : 173 (m^+, 100%), 172 (45), 158 (20), 131 (15), 93 (55), 81 (25), 78 (15).

(xxii) 1,1-{(Pyridin-2-yl)(N-methylimidazol-2-yl)}ethan-1-ol, pymimCMeOH.

To a cooled (-50°C) solution of N-methylimidazole (7.5cm^3, 0.095mol) in anhydrous diethyl ether (100cm^3) under N_2 was added phenyllithium (Li : 1.32gm, BrPh : 9.9cm^3). The resulting suspension was allowed to warm slowly to -10°C over *ca.* 1 hour, producing a solution virtually free from all solids. To the recooled (-60°) solution was added dropwise 2-acetylpyridine (10.0cm^3, 0.09mol) dissolved in diethyl ether (10cm^3). A thick white suspension formed slowly, which was warmed slowly to room temperature, followed by continued reaction at room temperature for 2 hours. The suspension was hydrolysed with 30cm^3 of 5M HCl, and the organic and aqueous phases separated, followed by extraction of the organic phase with 5M HCl (2x5cm^3). The combined aqueous phases were basified (Na_2CO_3), and continuously extracted with chloroform for 12 hours. The chloroform extract was then dried ($MgSO_4$), filtered, and evaporated to yield a brown oil. Distillation of the oil under high vacuum gave a mixture of N-methylimidazole and 2-acetylpyridine (^{1}H N.M.R. identification).

The residue was taken up into chloroform and passed, with the aid of a vacuum, through a short silica column, evaporation afforded a yellow oil which crystallised on standing. Recrystallisation was effected from dichloromethane/hexane, with cooling, to afford the desired compound, pymimCMeOH {11.6 gm, 64%; m.pt. 46-49°C} as white plates.

Analysis; was not obtained as pymimCMeOH is an intermediate in the preparation of pymimC=CH_2 and pymimCHMe.

^{1}**H N.M.R.**, Chloroform-D;

py resonances, 8.56, ddd, H_6 ($^3J_{5,6}$=4.92, $^4J_{4,6}$=1.59, $^5J_{3,6}$=0.99 Hz), 1H; 7.67, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.75, $^4J_{4,6}$=1.74 Hz), 1H; 7.25, m, H_5, 1H; 7.13, m, H_3 ($^3J_{3,4}$=8.01 Hz), 1H.

mim resonances, 6.96, d, $H_{4(5)}$ ($^3J_{4,5}$=1.20 Hz), 1H; 6.77, d, $H_{5(4)}$ ($^3J_{4,5}$=1.17 Hz), 1H; 3.35, s, N**Me**, 3H.

6.07, s, COH, 1H; 1.98, s, C**Me**, 3H.

Infrared, nujol;

3000 , 1648, 1282, 1220, 1156, 1130, 1090, 1072, 934, 792, 764, 730, 672, 626, 586 cm^{-1}.

Mass Spectrum;

m/e (I%) : 203 (M^+, 30%), 188 (95), 184 (20), 160 (20), 125 (95), 122 (30), 106 (50), 93 (20), 78 (100).

(xxiii)1,1-{(Pyridin-2-yl)(N-Methylimidazol-2-yl)}ethene, pymimC=CH_2.

Dehydration of pymimCMeOH to pymimC=CH_2 was achieved by an analogous method to that described above for the preparation of $py_2C=CH_2$. Passage through a silica column, followed by evaporation of chloroform gave a yellow oil {76%}.

Analysis, was not attempted.

^{1}H N.M.R., Acetone-D6;

py resonances, 7.58, ddd, H_6 ($^3J_{5,6}$=4.61, $^4J_{4,6}$=1.65, $^5J_{3,6}$=0.89 Hz), 1H; 7.76, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.91, $^4J_{4,6}$=1.86 Hz), 1H; 7.31, m, H_3, H_5, 2H.

mim resonances, 7.13, d, $H_{4(5)}$ ($^3J_{4,5}$=0.95 Hz), 1H; 6.98, d, $H_{5(4)}$ ($^3J_{4,5}$=0.95 Hz), 1H; 3.50, s, **NMe**, 3H.

6.52, d, C=CHH (^2J=1.79 Hz), 1H; 5.70, d, C=CHH(^2J=1.80 Hz), 1H.

Infrared, thin film;

2948, 1586, 1566, 1488, 1470, 1432, 1408, 1304, 1304, 1282, 1136, 1108, 992, 924, 804, 760, 664, 622 cm^{-1}.

Mass Spectrum;

m/e (I%) : 185 (M^+, 50%), 184 (100), 142 (10), 107 (10), 107 (15), 78 (15).

(xxiv)1,1-{(Pyridin-2-yl)(N-Methylimidazol-2-yl)}ethane, pymimCHMe.

Hydrogenation of pymimC=CH_2 to give pymimCHMe was achieved by an identical method to that employed for the hydrogenation of $py_2C=CH_2$ to py_2CHMe. After filtration and evaporation of ethanol, the crude product was distiled at 132-144°C and 0.15 mmHg to give a clear, slightly yellow oil {79%}.

Analysis, was not attempted.

^{1}H N.M.R., Acetone-D6;

py resonances, 8.49, d, H_6 ($^3J_{5,6}$=4.44 Hz), 1H; 7.68, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.64, $^4J_{4,6}$=1.85 Hz), 1H; 7.20, ddd, H_5 ($^3J_{4,5}$~7.45, $^3J_{5,6}$=4.87, $^4J_{3,5}$=1.09 Hz), 1H; 7.11, m, H_3 ($^3J_{3,4}$=7.92 Hz), 1H.

mim resonances, 6.95, d, $H_{4(5)}$ ($^3J_{4,5}$=1.08 Hz), 1H; 6.86, d, $H_{5(4)}$ ($^3J_{4,5}$=1.08 Hz), 1H; 3.48, s, **NMe**, 3H.

4.42, q, CHMe (^3J=7.20 Hz), 1H; 1.69, d, **CHMe** (^3J=7.20 Hz), 1H.

Infrared, thin film;

2976, 1592, 1570, 1520, 1494, 1472, 1434, 1414, 1414, 1230, 1140, 1062, 1046, 994, 918, 752, 720, 590 cm^{-1}.

Mass Spectrum;

m/e (I%) : 187 (M^+, 75%), 186 (40), 172 (25), 109 (100), 106 (20), 93 (25), 78 (20).

(xxv) {(Pyridin-2-yl)bis(Pyrazol-1-yl)}methane, $pypz_2CH$, was prepared by the method of Canty and Honeyman.[11]

The procedure followed was identical to that described below for the preparation of $mimpz_2CH$, except for substitution of 2-pyridinecarbaldehyde, pyCOH, for mimCOH, and inclusion of $CoCl_2$ catalyst.[17]

^1H N.M.R., Acetone-D6;

py resonances, 8.61, ddd, H_6 ($^3J_{5,6}$=4.83, $^4J_{4,6}$=1.80, $^5J_{3,6}$=0.94 Hz), 1H; ~7.85, m, H_4 (obs.), 1H; 7.42, ddd, H_5 ($^3J_{4,5}$=7.59, $^3J_{3,4}$=4.81, $^4J_{3,5}$=0.73 Hz), 1H; 7.15, d, H_3 ($^3J_{3,4}$=7.92 Hz), 1H.

pz resonances, ~7.85, m, H_5 ($^3J_{4,5}$~2.03 Hz), 2H; 7.57, d, H_3 ($^3J_{3,4}$=1.73 Hz), 2H; 6.36, dd, H_4 ($^3J_{4,5}$=2.36, $^3J_{3,4}$=1.88 Hz), 2H.

7.88, s, CH, 1H.

(xxvi){(N-Methylimidazol-2-yl)bis(Pyrazol-1-yl)}methane, $mimpz_2CH$

To solid bis(pyrazol-1-yl)methanone (2.5gm, 0.015mol) under a N_2 atmosphere was added, with stirring, N-methyl-2-imidazolecarbaldehyde[25] (mimCOH, 1.65gm, 0.015mol). A vigorous reaction began immediately to produce a red-brown tar and a gas, presumably CO_2. On completion of the reaction the tar formed was taken up into dichloromethane and purified by column chromotography (silica gel, medium pressure, dichloromethane elution), giving a clear, colourless eleut; all other components remained on the baseline or had very low R_f values. Addition of hexane and slow removal of dichloromethane, under a vacuum at ambient temperature, gave the desired product, $mimpz_2CH$ {1.7gm, 49%, m.pt. 104-106°C}, as white crystals.

Analysis;

found %	: C	57.89	H	5.36	N	37.02
calc. %	: C	57.88	H	5.30	N	36.82

^{1}H N.M.R., Acetone-D6;

pz resonances, 7.93, d, H_5 ($^3J_{4,5}$=2.56 Hz), 2H; 7.52, s, H_3, 2H; 6.33, dd, H_4 ($^3J_{4,5}$=2.46, $^3J_{3,4}$=1.83 Hz), 2H.

mim resonances, 7.16, d, $H_{4(5)}$ ($^3J_{4,5}$=1.08 Hz), 1H; 6.95, d, $H_{5(4)}$ ($^3J_{4,5}$=1.11 Hz), 1H; 3.56, s, NMe, 3H.

8.00, s, CH, 1H.

Infrared, Nujol;

1296, 1284, 1222, 1208, 1168, 1078, 1038, 970, 858, 814, 798, 762, 744, 628 cm^{-1}

Mass Spectrum;

m/e (I%) : 228 (M^+, 15%), 227 (25), 161 (100), 160 (15), 124 (10), 68 (10).

(xxvii){(Pyridin-2-yl)bis(N-Methylimidazol-2-yl)}methane, pymim$_2$CH.

To a cold (0°C) suspension of bis(N-methylimidazol-2-yl)methane (mim_2CH_2, 4.0gm, 0.023mol) in anhydrous tetrahydrofuran (20cm^3) under a N_2 atmosphere was added phenyllithium (Li : 0.35gm, BrPh : 2.63cm^3). The suspension began to clear immediately, and after *ca.* 30 minutes a clear red solution had formed, to which was added 2-bromopyridine (2.38cm^3, 0.023mol) dissolved in diethyl ether (10cm^3). Stirring at 0°C was continued for 30 minutes, followed by addition of toluene (100cm^3), and removal of diethyl ether by distillation. The toluene volume was made up to *ca.* 200cm^3, and the mixture heated at 110°C for 12 hours. The suspension formed was hydrolysed with the minimum quantity of water required to dissolve suspended salts, and the organic and aqueous phases separated, followed by extraction of the organic phase with 4M HCl (5x5cm^3). The combined aqueous phases were then basified with Na_2CO_3, extracted into chloroform (10x5cm^3), and dried over $MgSO_4$. Evaporation, preceded by filtration, gave a brown oil. Dissolution into chloroform and passage through a short silica column, followed by addition of hexane

gave, upon standing, the desired compound, $pymim_2CH$ {2.75gm, 48%, m.pt 137-138°C}, as cream crystals.

Analysis;

found %	: C	66.15	H	5.94	N	27.54
calc. %	: C	66.38	H	5.97	N	27.65

^{1}H N.M.R., Acetone-D6

py resonances, 8.48, m, H_6 ($^3J_{5,6}$=4.89 Hz), 1H; 7.74, ddd, H_4 ($^3J_{4.5}$~$^3J_{3,4}$~7.74, $^4J_{4,6}$=1.77 Hz), 1H; 7.26, m, H_3, H_5, 2H.

mim resonances, 7.02, d, $H_{4(5)}$ ($^3J_{4,.5}$=1.17 Hz), 2H; 6.81, d, $H_{5(4)}$ ($^3J_{4,5}$=1.18 Hz), 2H; 3.50, s, **NMe**, 6H. 6.02, s, **CH**, 1H.

Infrared, nujol;

1594, 1570, 1494, 1408, 1280, 1150, 1134, 1082, 996, 770, 732, 698, 614 cm^{-1}.

Mass Spectrum;

m/e (I%) : 253 (M^+, 100%), 252 (15), 175 (20), 172 (15), 161 (40), 158 (80), 96 (60), 95 (20), 78 (15).

(xxviii){(N-Methylimidazol-2-yl)bis(Pyridin-2-yl)}methane, $mimpy_2CH$, was prepared from $mimpy_2CH_2$ by a similar method to that outlined above, with the following modifications:

After addition of 2-bromopyridine, and toluene/diethyl ether exchange, the mixture was heated at 110°C for *ca.* 24 hours. Work-up proceeded as above, except, prior to passage of the oil (dissolved in chloroform) through a silica column, the oil was distilled under high vacuum to remove unreacted 2-bromopyridine (20-25°C, 0.1 mmHg) and $mimpyCH_2$ (105-115°C, 0.1 mmHg). The desired compound, $mimpy_2CH$ {23%; m.pt. 79-81°C} was recrystallised from dichloromethane/hexane to give cream crystals.

Analysis;

found %	: C	71.83	H	5.67	N	22.33
calc. %	: C	71.98	H	5.64	N	22.38

^{1}H N.M.R., Acetone-D6;

py resonances, 8.48, ddd, H_6 ($^3J_{5,6}$=4.83, $^4J_{4,6}$=1.74, $^5J_{3,6}$=0.90 Hz), 2H; 7.72, ddd, H_4 ($^3J_{4,5}$~$^3J_{3,4}$~7.69, $^4J_{4,6}$=1.83 Hz), 2H; 7.39, d, H_3 ($^3J_{3,4}$=7.94 Hz), 2H; 7.23, ddd, H_5 ($^3J_{4,5}$=7.50, $^3J_{5,6}$=4.86, $^4J_{3,5}$=1.08 Hz), 2H.

mim resonances, 7.02, d, $H_{4(5)}$ ($^3J_{4,5}$=1.14 Hz), 1H; 6.84, d, $H_{5(4)}$ ($^3J_{4,5}$=1.12 Hz), 1H; 3.60, s, **NMe**, 3H.

5.95, s, **CH**, 1H.

Infrared, nujol;

1588, 1570, 1282, 1168, 1148, 1128, 1086, 994, 772, 740 cm^{-1}.

Mass Spectrum;

m/e (I%) : 250 (M^+, 100%), 249 (30), 172 (20), 168 (30), 158 (60), 78 (20).

(xxix) 2,2'-Bipyridyl, 1,10-phenanthroline, and 2,2':6',2"-Terpyridyl were obtained from commercial sources.

^{1}H N.M.R., Acetone-D6.

2,2'-bipyridyl (bipy), 8.68, ddd, H_6 ($^3J_{5,6}$=4.77, $^4J_{4,6}$=1.74, $^5J_{3,6}$=0.88 Hz), 2H; 8.59, d, H_3 ($^3J_{3,4}$=7.98 Hz), 2H; 7.93, ddd, ($^3J_{4,5}$~$^3J_{3,4}$~7.73, $^4J_{4,6}$=1.81 Hz), 2H; 7.41, ddd, H_5 ($^3J_{4,5}$=7.61, $^3J_{5,6}$=4.74, $^4J_{3,5}$=1.22 Hz), 2H.

1,10-phenanthroline (phen), 9.12, dd, $H_{2,9}$ ($^3J_{2,3}$=4.26, $^4J_{2,4}$=1.77 Hz), 2H; 8.46, dd, $H_{4,7}$ ($^3J_{3,4}$=8.10, $^4J_{2,4}$=1.77 Hz), 2H; 7.97, s, $H_{5,6}$, 2H; 7.75, dd, $H_{3,8}$ ($^3J_{3,4}$=8.10, $^3J_{2,3}$=4.29 Hz), 2H.

2,2':6',2"-terpyridyl (terpy)($CDCl_3$), 8.57, ddd, $H_{6,6"}$ ($^3J_{5,6}$=4.83, $^4J_{4,6}$=1.80, $^5J_{3,6}$=0.90 Hz), 2H; 8.49, m, $H_{3,3"}$ ($^3J_{3,4}$=7.98 Hz), 2H; 7.72, ddd, $H_{4,4"}$ ($^3J_{4,5}$~$^3J_{3,4}$*f*7.50, $^4J_{4,6}$=1.80 Hz), 2H; 7.20, ddd, $H_{5,5"}$ ($^3J_{4,5}$=7.44, $^3J_{5,6}$=4.80, $^4J_{3,5}$=1.20 Hz), 2H; 8.32, d, $H_{3',5'}$ (^3J=7.86 Hz), 2H; 7.83, t, $H_{4'}$ (^3J=7.80 Hz), 1H.

References

1. Perrin, D.D., Armarego, W.L.F., and Perrin, O.R.,
"Purification of Laboratory Chemicals", (2nd Ed), Pergamon, 1980.

2. Pyridazine is commercially available or may be readily prepared by the method of:
Mizzoni, R.H., and Spoerri, P.E.,
J. Am. Chem. Soc., **73** (1951) 1873.

3. Harlety, F.R.,
Organomet. Chem. Rev. A., **6** (1970) 119.

4. Goggin, P.L., Goodfellow, R.J., Haddock, S.R., Reed, F.J.S., Smith, J.G., and Thomas, K.M.,
J. Chem. Soc. Dalton Trans., (1972) 1904.

5. Lipton, M.F., Sorensen, C.M., and Sadler, A.C.,
J. Organomet. Chem.,**186** (1980) 155.

6. Gilman, H., Zoellner, E.A., and Selby, W.M.,
J. Am. Chem. Soc., 55 (1933) 1252.

7. Lusch, M.J., Phillips, W.V., Sieloff, R.F., Nomura, G.S., and House, H.O.,
Org. Synth., **62** (1984) 101.

8. Kamienski, C.W., and Esmay, D.L.,
J. Org. Chem., 25 (1960) 1807.

9. Jones, R.G., and Gilman, H.,
Org. React., **6** (1951) 339.

10. Gilman, H., and Sptaz, S.M.,
J. Org. Chem., **16** (1951) 1485.

11. Canty, A.J., and Honeyman, R.T., Unpublished results.

12. Calvin, G., and Coates, G.E.,
J. Chem. Soc., (1960) 2008.

13. Milstein, D., and Stille, J.K.,
J. Am. Chem. Soc., **101** (1979) 4981.

14. Gillie, A., and Stille, J.K.,
J. Am. Chem. Soc., **102** (1980) 4933.

15. Chaudhur, N., Kekre, M.G., and Puddephatt, R.J.,
J. Organomet.Chem.., **73** (1974) C17.

16. Julia, S., Sala, P., del Mazo, J., Sancho, M., Ochoa, C., Elguero, J., Fayet, J.P., and Vertut, M.C.,
J. Heterocycl. Chem., **19** (1982) 1141.

17. The, K.I., and Peterson, L.K.,
Can. J. Chem., **51** (1973) 422.

18. The, K.I., Peterson, L.K., and Kiehlmann, E.,
Can. J. Chem., **51** (1973) 2448.
Or may be prepared in lower yield by the Method of Trojimenko,
J. Am. Chem. Soc., **92** (1970) 5118.

19. Newkome, G.R., Gupta, V.K., Taylor, H.C.R., and Fronczek, F.R.,
Organometallics, **3** (1984) 1549.

20. Alternatively, py_2CHMe may be prepared by the method of
Minchin, N.J., Ph.D. Thesis, University of Tasmania, 1986.

21. Canty, A.J., Chaichit, N., Gatehouse, B.M., George, E.E., and Hayhurst, G.,
Inorg. Chem., **20** (1981) 2414.

22. mim_2C0 may also be prepared by the method of
Gorun, S.M., Papaefthymiou, G.C., Frankel, R.B., and Lippard, S.J.,
J. Am. Chem. Soc., **109** (1987) 4244.
or
Regel, E., and Buchel, K.H.,
Liebigs Ann. Chem., (1977) 145.

23. $mimCH_2Cl.HCl$ was prepared by a similar method to that described by Jones, R.G.,
J. Am. Chem. Soc., **71** (1949) 383.

24. Canty, A.J., George, E.E., and Lee, C.V., *Aust. J. Chem.*, **36** (1983) 415.

25. mimCOH prepared by the method of, Iversen, P.E., and Henning, L., *Acta Chemica Scand.*, **20** (1966) 2649.

LIST OF PUBLICATIONS

1. Methylpalladium(II) Complexes of Pyrazole and Thioether Donor Ligands.
   Peter K. Byers and Allan J. Canty.
   Inorg. Chim. Acta, **104** (1985) L13.

2. Synthesis, Spectroscopic and Structural Studies of the Methylpalladium(II) Complexes $[\{PdMe(SMe_2)X\}_2]$ (X=Cl, Br or I); Crystal Structure of *trans*-$[\{PdMe(SMe_2)(\mu\text{-}Cl)\}_2]$.
   Peter K. Byers, Allan J. Canty, Lutz M. Engelhardt and Allan H. White.
   J. Chem. Soc. Dalton Trans., (1986) 1731.

3. The Oxidative Addition of Iodomethane to $[PdMe_2(bpy)]$ and the X-Ray Structure of the Organopalladium(IV) Product *fac*-$[PdMe_3I(bpy)]$ (bpy=2,2'-bipyridyl).
   Peter K. Byers, Allan J. Canty, Brian W. Skelton and Allan H. White.
   J. Chem. Soc., Chem. Commun., (1986) 1722.

4. Synthesis of the First Organopalladium(IV) Cations, including the First X-Ray Study of Isostructural Organopalladium(IV) and Platinum(IV) Complexes, [*fac*-$MMe_3\{$tris(pyrazol-1-yl)methane-N,N'N"$\}$]I.
   Peter K. Byers, Allan J. Canty, Brian W. Skelton and Allan H. White.
   J. Chem. Soc., Chem. Commun., (1987) 1093.

5. Convenient Synthetic Routes to MePd(II), Me_2Pd(II), and Me_3Pd(IV) Complexes. The Crystal Structure of the MePd(II) Complex [MePd(2,2'-bipyridyl)(γ-picoline)]BF_4.
   Peter K. Byers, Allan J. Canty, Brian W. Skelton and Allan H. White.
   J. Organomet. Chem., **336** (1987) L55.

6. Reactivity and Mechanism in Oxidative Addition to Palladium(II) and Reductive Elimination from Palladium(IV), and an Estimate of the Palladium-Methyl Bond Energy.
   Peter K. Byers, Allan J. Canty, Margarita Crespo, Richard J. Puddephatt and John D. Scott.
   Organometallics, **7** (1988) 1363.

7. Organopalladium(IV) Chemistry: Ethyl, η^1-Benzyl, and η^1-Allyl Systems.
   Peter K. Byers and Allan J. Canty.
   J. Chem. Soc., Chem. Comm., (1988) 639.

Methylpalladium(II) Complexes of Pyrazole and Thioether Donor Ligands

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Organopalladium(II) species RPd(II), $R_2Pd(II)$, and RR'Pd(II) are believed to occur in a wide range of catalytic systems of importance in synthesis of organic compounds involving coupling to form R–R and R–R' [1, 2]. Although many methylpalladium(II) complexes of phosphorus and arsenic donor ligands have been synthesized [3], reports of complexes containing nitrogen and thioether donor ligands are restricted to the 2,2'-bipyridyl derivatives $Me_2Pd(bpy)$ [4] and Me(X)Pd(bpy) (X = Cl [5], I [6]) and the dithioether derivatives $Me_2Pd(RSCH_2CH_2SR)$ (R = Me, Et) [4]. Simple methyl complexes are of interest as models for intermediates in catalytic systems, and also as models for the synthesis of organic compounds via palladation of organic compounds involving neutral donor ligand directing groups, usually nitrogen donors [1, 3].

We report here initial studies of the synthesis and reactivity of a series of complexes $Me_2Pd(L)$ and Me(I)Pd(L) [L = poly(pyrazol-1-yl)methane ligands pz_2CH_2, $pz_2C(II)Me$, pz_2CMe_2, and pz_3CH], together with the synthesis of $[Me(I)Pd(SMe_2)]_2$.

$$PdCl_2(SMe_2)_2 \xrightarrow[\text{(ii) L}]{\text{(i) 2-3 MeLi(halide free, } -60\ ^\circ C)} Me_2Pd(L)$$

$$PdCl_2(SMe_2)_2 \xrightarrow[\text{(ii) L}]{\text{(i) 2 MeMgI } (-40\ ^\circ C)} Me(I)Pd(L)$$

$$PdCl_2(SMe_2)_2 \xrightarrow{\text{2 MeLi/LiI } (-60\ ^\circ C)} [Me(I)Pd(SMe_2)]_2$$

In a typical synthesis of $Me_2Pd(L)$, 2–3 mol equivalents of halide free methyllithium were reacted with *trans*-$PdCl_2(SMe_2)_2$ at −60 °C in dry diethyl ether under nitrogen until the solution clarified, solid L was added and the solution slowly warmed with stirring to −15 °C, followed by hydrolysis, filtration, separation and drying of the organic layer, filtration, removal of solvent to dryness, and recrystallization of $Me_2Pd(L)$ from dry acetone/hexane at −70 °C. Similar procedures were used for synthesis of Me(I)Pd(L) and $[Me(I)Pd(SMe_2)]_2$, with the latter synthesis employing MeLi containing LiI (prepared from 2Li + MeI in diethyl ether) and isolation of the complex directly from diethyl ether after hydrolysis.

The complexes have satisfactory microanalyses (C, H, N, I, S), infrared, and ^1H NMR spectra. For example, complexes with pz_3CH exhibit variable temperature ^1H NMR spectra, with $Me_2Pd(pz_3CH)$ giving six pyrazole ring resonances at −60 °C in $(CD_3)_2CO$ in the ratio 1:2:2:1:2:1 corresponding to two coordinated rings and one uncoordinated (or weakly coordinated) ring, with coalescence of resonances at higher temperatures consistent with rapid intramolecular exchange of coordinated and uncoordinated rings.

The complex $[Me(I)Pd(SMe_2)]_2$ is assigned a dimeric structure from osmometric molecular weight measurements, giving a value of 679 (Calc. for dimer 621) on initial dissolution in chloroform at 37 °C prior to decomposition. An analogous platinum complex has been detected by ^1H NMR spectroscopy in $CDCl_3$, but could not be isolated [7]. Variable temperature studies and interpretation of ^1H–^{195}Pt coupling allowed assignment of structure as $[Me(\mu\text{-}I)Pt(SMe_2)]_2$, with presence of *cis* and *trans* isomers in rapid equilibrium [7]. The palladium complex, and the analogous chloride, $[Me(Cl)Pd(SMe_2)]_2$, obtained from *trans*-$PdCl_2(SMe_2)_2$ and halide free MeLi, have much simpler spectra, lacking coupling, with MePd(II) singlets [δ 0.76 (Cl), 0.93 (I)] and SMe_2 singlets [2.34 (Cl), 2.37 (I)] in 1:2 ratio, unaltered on cooling to −60 °C in $CDCl_3$. Thus, ^1H NMR spectra do not permit definite assignment of structure.

The complexes Me(I)Pd(L) are quite stable at ambient temperature, $Me_2Pd(L)$ require storage at −20 °C, and the dimethylsulfide complexes slowly decompose over 2–3 months at −20 °C. Preliminary studies of the reactivity of the complexes indicate that $[Me(I)Pd(SMe_2)]_2$, which is readily obtained in 85% yield, may be a suitable reagent for synthesis of methylpalladium(II) complexes, *e.g.* it reacts directly with $pz_2CH(Me)$ and pz_2CMe_2 to form Me(I)Pd(L). The pyrazole complexes may also be suitable for modelling reactions that may be involved in catalytic systems, *e.g.* iodomethane reacts cleanly with $Me_2Pd(pz_2CMe_2)$ to form Me(I)-$Pd(pz_2CMe_2)$. Further studies of synthetic applications and reactivity of the complexes are in progress.

Acknowledgements

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0020-1693/85/$3.30

References

1 B. M. Trost and T. R. Verhoeven, in G. Wilkinson (ed.), 'Comprehensive Organometallic Chemistry, Vol. 8', Pergamon, London, 1982, p. 799.
2 A. Yamamoto, T. Yamamoto, S. Komiya and F. Ozawa, *Pure Appl. Chem.*, *56*, 1621 (1984).
3 P. M. Maitlis, P. Espinet and M. J. H. Russell, in G. Wilkinson (ed.), 'Comprehensive Organometallic Chemistry, Vol. 6', Pergamon, London, 1982, p. 279.
4 G. Calvin and G. E. Coates, *J. Chem. Soc.*, 2008 (1960).
5 N. Chaudhury, M. G. Kekre and R. J. Puddephatt, *J. Organomet. Chem.*, *73*, C17 (1974).
6 P. M. Maitlis and F. G. A. Stone, *Chem. Ind.*, 1865 (1962).
7 J. D. Scott and R. J. Puddephatt, *Organometallics*, *2*, 1643 (1983).

Synthesis, Spectroscopic, and Structural Studies of the Methylpalladium(II) Complexes $[\{PdMe(SMe_2)X\}_2]$ (X = Cl, Br, or I); Crystal Structure of *trans*-$[\{PdMe(SMe_2)(\mu\text{-}Cl)\}_2]$ †

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The complexes $[\{PdMe(SMe_2)X\}_2]$ (X = Cl, Br, or I) have been prepared by reaction of *trans*-$[Pd(SMe_2)_2X_2]$ with halide-free methyl-lithium (X = Cl or Br), and reaction of *trans*-$[Pd(SMe_2)_2Cl_2]$ with methyl-lithium containing lithium iodide (X = I) in diethyl ether at −60 to −15 °C under nitrogen. Other synthetic routes to the bromo- and iodo-complexes are also described. The crystal structure of the chloro-complex $[\{PdMe(SMe_2)(\mu\text{-}Cl)\}_2]$ has been determined by single-crystal *X*-ray diffraction at 295 K and refined by least-squares methods to $R = 0.025$ for 1 914 independent 'observed' reflections [space group $P2_1/n$, $a = 10.792(4)$, $b = 7.373(2)$, $c = 9.131(5)$ Å, $\beta = 109.03(3)°$, and $Z = 2$]. The centrosymmetric dimeric molecules have *trans* stereochemistry with bridging chloro-groups and square-planar geometry for palladium(II). ^1H N.m.r. and far-i.r. spectra, and molecular weight determinations are consistent with similar structures for the bromo- and iodo-complexes.

Palladium(II) chloride and bromide complexes of dimethyl sulphide with a PdX_2:SMe_2 ratio of 1:1 are known to be dimeric with bridging halogeno-groups, *trans*-$[\{PdX(SMe_2)(\mu\text{-}X)\}_2]$ (**1a**), from vibrational and ^1H n.m.r. spectroscopic studies (X = Cl or Br),[1,2] and an *X*-ray crystallographic study (X = Br).[3,4] Platinum(II) exhibits different behaviour, with vibrational spectra indicating bridging iodo-groups for *trans*-$[\{PtI(SMe_2)(\mu\text{-}I)\}_2]$ (**1b**),[5] as for the palladium(II) chloro- and bromo-complexes, but bridging thioether for $[\{PtX_2(\mu\text{-}SMe_2)\}_2]$ (X = Cl or Br) (**2**),[3,5] as shown crystallographically for $[\{PtBr_2(\mu\text{-}SEt_2)\}_2]$.[3,4]

Methylmetal(II) complexes $[\{MMe(SMe_2)X\}_2]$ (M = Pd or Pt) may conceivably show related structural isomerism, and indeed ^1H n.m.r. spectroscopic studies have shown that $[\{PtMe(SMe_2)I\}_2]$, which could not be isolated as a solid, has iodo-bridging in chloroform with *cis*-(**3a**) and *trans*-(**3b**) isomers in equilibrium.[6] Analogous palladium(II) complexes have been obtained during development of syntheses of methylpalladium(II) poly(pyrazol-1-yl)methane complexes from *trans*-$[Pd(SMe_2)_2Cl_2]$,[7] and we report here the synthesis of $[\{PdMe(SMe_2)X\}_2]$ (X = Cl, Br, or I), an *X*-ray structural study of *trans*-$[\{PdMe(SMe_2)(\mu\text{-}Cl)\}_2]$, and vibrational spectroscopic studies indicating that the bromo- and iodo-derivatives have the same structure as the chloro-derivative in the solid state.

Results

Preparation and Characterization of Complexes.—The complexes $[\{PdMe(SMe_2)X\}_2]$ (X = Cl or Br) were prepared in diethyl ether under nitrogen at low temperature (−60 °C initially, slowly warmed to *ca.* −15 °C) by reaction of *trans*-$[Pd(SMe_2)_2X_2]$ with one mol equivalent of 'halide-free methyl-lithium' (containing 0.4% LiCl), followed by hydrolysis and isolation of the complexes from diethyl ether [equation (1)]. *trans*-$[Pd(SMe_2)_2I_2]$ has low stability,[2] and it was found that $[\{PdMe(SMe_2)I\}_2]$ may be conveniently prepared by reaction of *trans*-$[Pd(SMe_2)_2Cl_2]$ with methyl-lithium–lithium iodide (from MeI + 2Li) under similar conditions to those used for the chloro- and bromo-complexes [equation (2)]; the bromo-complex may also be obtained in this manner using methyl-lithium–lithium bromide.

$$trans\text{-}[Pd(SMe_2)_2X_2] \xrightarrow{LiMe} \tfrac{1}{2}[\{PdMe(SMe_2)X\}_2] \quad (X = Cl \text{ or } Br) \quad (1)$$

$$trans\text{-}[Pd(SMe_2)_2Cl_2] \xrightarrow{2LiMe\text{-}LiX} \tfrac{1}{2}[\{PdMe(SMe_2)X\}_2] \quad (X = Br \text{ or } I) \quad (2)$$

In addition, the bromo- and iodo-complexes may be prepared by exchange reactions in diethyl ether–water [equation (3)], and on reaction of MeX with dimethylpalladium(II) species obtained[7] from *trans*-$[Pd(SMe_2)_2Cl_2]$ and two mol equivalents of halide-free methyl-lithium [equation (4)].

$$[\{PdMe(SMe_2)X\}_2] \xrightarrow{2KY} [\{PdMe(SMe_2)Y\}_2] \quad (X = Cl, Y = Br \text{ or } I; X = Br, Y = I) \quad (3)$$

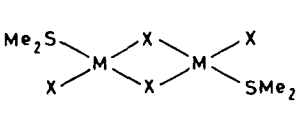
$$trans\text{-}[Pd(SMe_2)_2Cl_2] \xrightarrow[(ii)\ MeX]{(i)\ 2LiMe} \tfrac{1}{2}[\{PdMe(SMe_2)X\}_2] \quad (X = Br \text{ or } I) \quad (4)$$

Although the complexes slowly decompose at ambient temperature, and on dissolution in chloroform, they gave satisfactory microanalyses and molecular weight values in chloroform, and both the near-i.r. and ^1H n.m.r. spectra are very similar (Table 1). However, far-i.r. spectra (Table 2) are radically different, as expected, since this region contains palladium–halogen stretching frequencies.

Crystal Structure of $[\{PdMe(SMe_2)(\mu\text{-}Cl)\}_2]$.—In the solid state, molecules of *trans*-$[\{PdMe(SMe_2)(\mu\text{-}Cl)\}_2]$ are situated at centres of symmetry in space group $P2_1/n$, with the maximum deviation (0.077 Å) from the $PdCl_2SC$ mean plane being

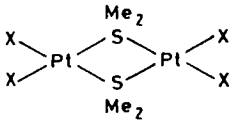
† *trans*-Di-μ-chloro-bis[(dimethyl sulphide)methylpalladium(II)].

Supplementary data available (No. SUP 56527, 3 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

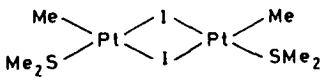


(1a) M = Pd; X = Cl or Br

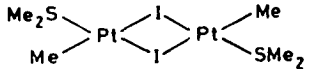
(1b) M = Pt; X = I



(2) X = Cl or Br



cis-[{PtMe(SMe$_2$)(μ-I)}$_2$] (3a)



trans-[{PtMe(SMe$_2$)(μ-I)}$_2$] (3b)

Table 1. Characterization data for the complexes

Complex	Colour	Analysis[a] (%) C	H	M[a,b,c]	^{1}H N.m.r.[c,d] PdMe	SMe$_2$	I.r.[e] (cm^{-1})
[{PdMe(SMe$_2$)(μ-Cl)}$_2$]	Yellow	16.6 (16.5)	3.7 (4.1)	448 (438)	0.78(1)	2.34(2)	2 952mw, 2 912mw, 2 880mw, 1 428s, 1 320mw, 1 304mw, 1 154m, 1 034m, 988m, 750m, 537w
[{PdMe(SMe$_2$)Br}$_2$]	Orange-tan	13.8 (13.7)	3.4 (3.4)	584 (527)	0.87(1)	2.43(2)	2 988m, 2 912m, 2 892mw, 1 428s, 1 316m br, 1 152m, 1 028m, 986s br, 762mw, 537mw
[{PdMe(SMe$_2$)I}$_2$]	Yellow	11.9 (11.6)	2.8 (2.9)	679 (621)	0.93(1)	2.39(2)	2 976mw br, 2 908mw br, 1 414m br, 1 320m, 1 302mw, 1 142m, 1 028m, 980m br, 753mw, 522w

[a] Calculated values are given in parentheses. [b] Osmometrically, 3 × 10^{-2} mol dm^{-3} at 37 °C. [c] The complexes slowly decompose in chloroform. [d] Shifts are in p.p.m. from SiMe$_4$ for spectra of complexes in CDCl$_3$; given as chemical shift (relative intensity); all resonances are sharp singlets; unaltered at −60 °C. [e] Nujol and hexachlorobutadiene mulls between KBr plates, 4 000—500 cm^{-1}.

Table 2. I.r. spectra (500—100 cm^{-1}) of [{PdX(SMe$_2$)(μ-X)}$_2$][a] and [{PdMe(SMe$_2$)X}$_2$][b]

	[{PdCl(SMe$_2$)(μ-Cl)}$_2$]	[{PdMe(SMe$_2$)(μ-Cl)}$_2$]	[{PdBr(SMe$_2$)(μ-Br)}$_2$]	[{PdMe(SMe$_2$)Br}$_2$][c]	[{PdMe(SMe$_2$)I}$_2$][d]
Pd–S str. (terminal)	340ms	319w	336s	319w	309w
Pd–X str. (terminal)	360s		274s		
Pd–X str. (bridging)	308ms[e]	275vs	223s[e]	175vs	150vs[h]
Pd–X str. (bridging)	282s[f]	244s, br[g]	195ms[f]	157m	
SC$_2$ def.		~285w (sh)	295ms	288mw	280mw
CSPd def.	209m, br	211vs[i]	185 (sh)	195m	188w, br
Skeletal and lattice modes	151 (sh)	154vw	124 (sh)	134w	126w
	148ms	141vw	119m	119vw	111w
	132wm	105vw	109vw (sh)	105w	

[a] From ref. 2, as mulls in mixtures of Nujol and vaseline. [b] This work, as powdered polyethylene discs. [c] Very weak, broad absorptions at ~273, ~252, and ~224 cm^{-1}. [d] Weak, very broad absorption at 270—240 cm^{-1}. [e] *trans* to S. [f] *trans* to X. [g] Shoulder at ~235 cm^{-1}. [h] Unsymmetrical, broader base at low frequency. [i] Shoulder at 193w cm^{-1}.

observed for the carbon atom C(1) (Table 3, Figure 1). The palladium atoms have square-planar geometry with angles at palladium in the range 87.42(4)—93.6(1)°. The Pd_2Cl_2 group is almost symmetrical, with Pd–Cl distances differing by 0.14 Å.

Far-i.r. Spectra of the Complexes.—Far-i.r. spectra (500—100 cm^{-1}) of the complexes are shown in Figure 2, and presented together with reported spectra and assignments for the closely related inorganic complexes [{PdX(SMe$_2$)(μ-X)}$_2$] (X = Cl or Br) in Table 2. Spectra are readily assigned by comparison with assignments of Goggin *et al.*[2] for the inorganic complexes, assuming that the bromo- and iodo-complexes have bridging halogeno-groups as found for the chloro-complex [{PdMe(SMe$_2$)(μ-Cl)}$_2$]. Thus, [{PdMe(SMe$_2$)(μ-Cl)}$_2$] has only one absorption above 300 cm^{-1}, at 319 cm^{-1}, assigned as ν(Pd–S)$_{terminal}$ by comparison with [{PdCl(SMe$_2$)(μ-Cl)}$_2$] which has ν(Pd–S)$_{terminal}$ at 340 cm^{-1}. Similarly, the bromo- and iodo-derivatives exhibit only one absorption above 300 cm^{-1}, at similar values, 319 and 309 cm^{-1} respectively, and are thus readily assigned as ν(Pd–S)$_{terminal}$ for halogeno-bridged structures.

In comparing spectra of [{PdMe(SMe$_2$)X}$_2$] the most striking feature is a shift to lower frequency for the major absorption in the region 290—240 cm^{-1} for the chloro-derivative, to 180—150 cm^{-1} (X = Br) and 150 cm^{-1} (X = I). The absorptions are readily assigned as ν(Pd–X)$_{bridging}$, with the chloro- and bromo-derivatives giving absorptions at similar frequencies to ν(Pd–X)$_{bridging}$ for [{PdX(SMe$_2$)(μ-X)}$_2$]. The ratios ν(Pd–X)/ν(Pd–Cl) ~0.64 (X = Br) and ~0.57 (X = I) are

Table 3. Non-hydrogen atom molecular geometry for *trans*-[{PdMe(SMe$_2$)(μ-Cl)}$_2$]; distances in Å, angles in °; primed atoms are generated by the inversion centre at the centre of the dimer *

Pd–C(1)	2.016(4)	Pd–S	2.265(1)
Pd–Cl	2.358(1)	S–C(2)	1.792(4)
Pd–Cl'	2.498(1)	S–C(3)	1.799(4)
C(1)–Pd–Cl	90.9(1)	Pd–Cl–Pd'	92.58(4)
C(1)–Pd–Cl'	177.3(1)	C(2)–S–Pd	104.5(2)
C(1)–Pd–S	93.6(1)	C(3)–S–Pd	116.2(2)
Cl–Pd–Cl'	87.42(4)	C(2)–S–C(3)	99.3(2)
Cl–Pd–S	175.20(3)		
Cl'–Pd–S	88.16(4)		

* Atom deviations from the mean plane defined by PdCl$_2$SC(1) are Pd, 0.004; Cl, −0.033; Cl', 0.005; S, −0.035; C(1), 0.077; C(2), 1.658; C(3), −0.240 Å; the plane is given by $0.6179X - 0.4979Y + 0.3738Z = 0.014$ (standard significance index for coplanarity $\chi^2 = 2.649$) and the right-hand orthogonal Å frame (X,Y,Z) has X parallel to a, Z in the ac plane.

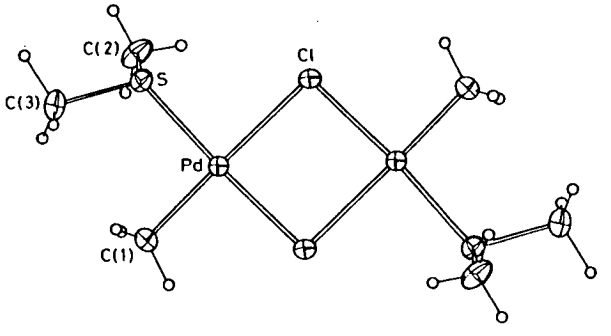


Figure 1. Structure of *trans*-[{PdMe(SMe$_2$)(μ-Cl)}$_2$] projected normal to the PdCl$_2$Pd plane; 20% thermal ellipsoids are shown for the non-hydrogen atoms, and hydrogen atoms are shown with an arbitrary radius of 0.1 Å

as expected,[8] *e.g.* ~0.7 for [{PdBr(SMe$_2$)(μ-Br)}$_2$] and ~0.6 for ν(Pd–I)$_{terminal}$ in *trans*-[PdI$_2$(SMe$_2$)$_2$].[2]

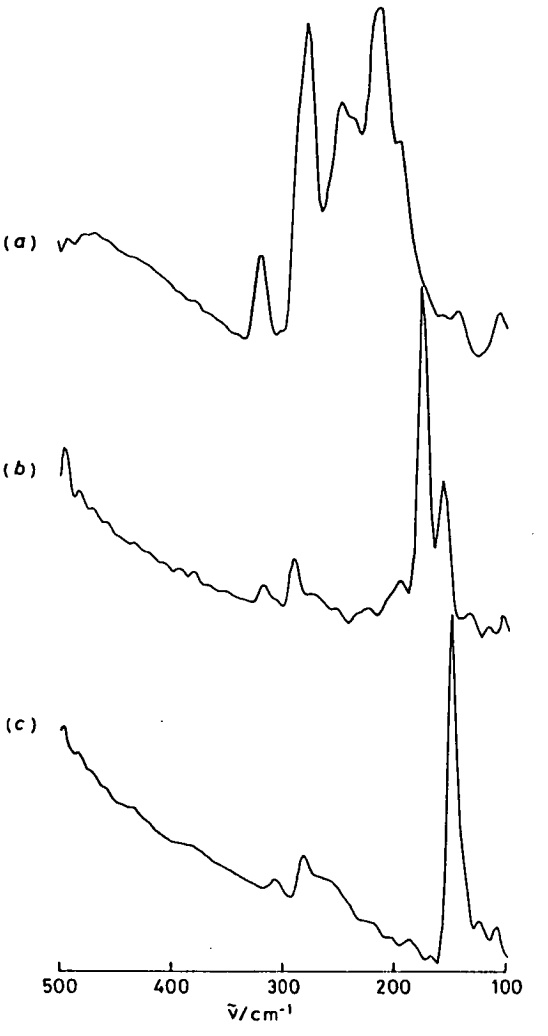


Figure 2. Far-i.r. spectra of [{PdMe(SMe$_2$)X}$_2$]: X = Cl (*a*), Br (*b*), or I (*c*)

Experimental

Microanalyses were by the Australian Microanalytical Service, far-i.r. spectra (500—100 cm^{-1}) were recorded with a Digilab FTS.20E Fourier-transform i.r. spectrometer, ^{1}H n.m.r. spectra in $CDCl_3$ were measured with a JEOL JNM-4H-100 spectrometer, and molecular weights were determined in chloroform at 37 °C with a Knauer vapour pressure osmometer.

Diethyl ether was dried over 4A molecular sieves, followed by reflux and distillation from sodium–benzophenone and storage over sodium. *trans*-[Pd(SMe$_2$)$_2$Cl$_2$] was prepared from *trans*-bis(benzonitrile)dichloropalladium(II) and dimethyl sulphide in benzene followed by recrystallization from hot ethanol; the dibromo-analogue was obtained on reaction of *trans*-[Pd(SMe$_2$)$_2$Cl$_2$] with KBr in acetone–water, and both complexes have far-i.r. spectra in agreement with those reported.[2] Methyl-lithium [diethyl ether solution, containing 0.4% LiCl (Ega) and diethyl ether solution, as complex with LiBr (Aldrich)] was standardized using 1,3-diphenyl-2-propanone tosylhydrazone[9] immediately prior to use in synthesis.

[{PdMe(SMe$_2$)(μ-Cl)}$_2$].—Methyl-lithium (0.4% LiCl solution, 1.85 cm^3, 2.3 mmol) was added to a suspension of *trans*-[Pd(SMe$_2$)$_2$Cl$_2$] (0.674 g, 2.2 mmol) in diethyl ether (70 cm^3) at −70 °C under nitrogen. The suspension was stirred for 1 h at −60 °C giving a colourless solution with some unreacted *trans*-[Pd(SMe$_2$)$_2$Cl$_2$], followed by gradual warming of the solution to −15 °C giving an orange solution with little unreacted reagent. After hydrolysis (2 cm^3) and filtration at −15 °C, subsequent evaporation of solvent in a vacuum at 0 °C gave a black solid. Extraction of the solid with dry acetone (4 × 5 cm^3), followed by addition of hexane (20 cm^3), and slow evaporation at 0 °C gave the product (0.22 g, 45%), m.p. 87 °C (decomp.). Recrystallization was not necessary, but may be achieved using acetone–light petroleum or acetone–water.

[{PdMe(SMe$_2$)Br}$_2$].—A similar procedure, using *trans*-[Pd(SMe$_2$)$_2$Br$_2$], gave the product in 70% yield, m.p. 104—105 °C (decomp.). Recrystallization was not necessary, but may be achieved using acetone–light petroleum. Alternatively, the bromo-complex may be prepared in a similar manner from *trans*-[Pd(SMe$_2$)$_2$Cl$_2$] and methyl-lithium–lithium bromide.

[{PdMe(SMe$_2$)I}$_2$].—To a suspension of lithium chips (0.118 g, 17 mmol) in diethyl ether (40 cm^3) under nitrogen was added iodomethane (0.1 cm^3), followed by dropwise addition of iodomethane (0.55 cm^3, 8.5 mmol) in diethyl ether (30 cm^3) over 30 min. The suspension was stirred until the lithium had been

consumed or reaction had ceased, followed by standardization.[9] Yields of methyl-lithium were commonly in the range 40—50%, and solutions were used immediately.

A similar procedure to that for the bromide gave an orange solution after hydrolysis (2 cm^3). After filtration, water (30 cm^3) was added and diethyl ether removed in a vacuum at 0 °C to give the product (85%), m.p. 120 °C (decomp.), which did not require recrystallization.

Synthesis of $[\{PdMe(SMe_2)X\}_2]$ *using Halide-free Methyl-lithium and Halogenomethane* (X = Br *or* I).—X = I. Methyl-lithium (0.4% LiCl solution, 3.5 cm^3, 2.9 mmol) was added to a suspension of *trans*-$[Pd(SMe_2)_2Cl_2]$ (0.417 g, 1.4 mmol) in diethyl ether (70 cm^3) at −70 °C under nitrogen. The suspension was stirred for 1 h at −60 °C giving a colourless solution, followed by warming to *ca.* −40 °C, addition of iodomethane (0.5 cm^3, 8 mmol), and gradual warming to −15 °C to give a yellow solution. Hydrolysis, followed by filtration and evaporation of diethyl ether at 0 °C gave the product (0.392 g, 91%).

X = Br. A similar procedure, involving warming to *ca.* 10 °C after addition of bromomethane, gave a black solution. Hydrolysis, followed by filtration gave a yellow solution that gave the product on evaporation of diethyl ether (41%).

Synthesis of $[\{PdMe(SMe_2)X\}_2]$ (X = Br *or* I) *from* $[\{PdMe(SMe_2)(\mu\text{-}Cl)\}_2]$ *and* KX.—On suspension of the chloro-complex in diethyl ether at −60 °C, KX (X = Br or I) was added and the resulting suspension allowed to warm slowly to *ca.* −10 °C. Water was added, and the diethyl ether slowly evaporated to yield the products (isolated by filtration).

Crystallography.—Crystals of *trans*-$[\{PdMe(SMe_2)(\mu\text{-}Cl)\}_2]$ were obtained by vapour-phase diffusion of diethyl ether into an acetone solution of the complex at −20 °C.

Crystal data. $(C_3H_9ClPdS)_2$, M = 438.0, monoclinic, space group $P2_1/n$ (variant of C_{2h}^5, no. 14), a = 10.792(4), b = 7.373(2), c = 9.131(5) Å, β = 109.03(3)°, U = 686.9(5) $Å^3$, D_c (Z = 2 dimers) = 2.12 g cm^{-3}, $F(000)$ = 424, monochromatic Mo-K_α radiation, λ = 0.710 69 Å, μ = 32 cm^{-1}. Specimen: 0.25 × 0.25 × 0.25 mm, transmission = 0.48 (min.), 0.53 (max.), $T \sim 295$ K.

Structure determination. A unique data set was measured to $2\theta_{max.} = 65°$ using a Syntex $P2_1$ four-circle diffractometer in conventional 2θ—θ scan mode, yielding 2 441 independent reflections, 1 914 with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after analytical absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; for the hydrogen atoms the corresponding isotropic form was constrained at an estimated value for each atom. At convergence, R and R' (statistical weights) quoted on $|F|$, were 0.025, 0.023. Neutral complex scattering factors were used.[10] Computation used the XTAL 83 program system[11] implemented by S. R. Hall on a Perkin-Elmer 3240 computer.

Atom co-ordinates are given in Table 4.

Table 4. Atom co-ordinates for *trans*-$[\{PdMe(SMe_2)(\mu\text{-}Cl)\}_2]$

Atom	x	y	z
Pd	0.094 24(2)	0.199 21(3)	0.035 40(2)
S	0.221 33(8)	0.320 16(10)	−0.094 10(8)
Cl	−0.047 27(8)	0.059 74(11)	0.151 09(8)
C(1)	0.134 1(4)	0.399 6(6)	0.194 2(4)
H(1A)	0.124(3)	0.506(5)	0.143(4)
H(1B)	0.222(4)	0.401(6)	0.238(4)
H(1C)	0.087(3)	0.376(6)	0.268(4)
C(2)	0.371 4(4)	0.194 5(6)	−0.026 6(6)
H(2A)	0.360(4)	0.063(6)	−0.029(5)
H(2B)	0.414(3)	0.198(5)	0.094(4)
H(2C)	0.420(4)	0.223(5)	−0.095(4)
C(3)	0.284 1(4)	0.544 2(5)	−0.035 9(5)
H(3A)	0.340(3)	0.538(5)	0.081(4)
H(3B)	0.223(4)	0.607(6)	−0.045(5)
H(3C)	0.352(4)	0.575(7)	−0.107(6)

Acknowledgements

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References

1 R. J. Goodfellow, P. L. Goggin, and L. M. Venanzi, *J. Chem. Soc. A*, 1967, 1897.
2 P. L. Goggin, R. J. Goodfellow, S. R. Haddock, F. J. S. Reed, J. G. Smith, and K. M. Thomas, *J. Chem. Soc., Dalton Trans.*, 1972, 1904.
3 P. L. Goggin, R. J. Goodfellow, D. L. Sales, J. Stokes, and P. Woodward, *Chem. Commun.*, 1968, 31.
4 D. L. Sales, J. Stokes, and P. Woodward, *J. Chem. Soc. A*, 1968, 1852.
5 P. L. Goggin, R. J. Goodfellow, and F. J. S. Reed, *J. Chem. Soc., Dalton Trans.*, 1974, 576.
6 J. D. Scott and R. J. Puddephatt, *Organometallics*, 1983, **2**, 1643.
7 P. K. Byers and A. J. Canty, *Inorg. Chim. Acta*, 1985, **104**, L13.
8 See for example, R. J. H. Clark, *Spectrochim. Acta*, 1965, **21**, 955.
9 M. F. Lipton, C. M. Sorensen, A. C. Sadler, and R. H. Shapiro, *J. Organomet. Chem.*, 1980, **186**, 155.
10 J. A. Ibers and W. C. Hamilton (eds.), 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
11 J. M. Stewart and S. R. Hall (eds.), 'The XTAL System,' Technical Report TR-1364, Computer Science Center, University of Maryland, 1983.

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The Oxidative Addition of Iodomethane to [$PdMe_2$(bpy)] and the *X*-Ray Structure of the Organopalladium(IV) Product *fac*-[$PdMe_3$(bpy)I] (bpy = 2,2′-bipyridyl)

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Oxidative addition of iodomethane to dimethyl(2,2′-bipyridyl)palladium(II) in acetone has resulted in isolation of the first hydrocarbylpalladium(IV) complex, *fac*-trimethyl(2,2′-bipyridyl)iodopalladium(IV); the complex has been structurally characterized, and reductively eliminates ethane in solution to form methyl(2,2′-bipyridyl)iodopalladium(II).

While platinum forms numerous organoplatinum(IV) complexes,[1a] with reports commencing in 1907,[2] organopalladium(IV) chemistry is represented only by the isolation of several mono- and bis-(pentafluorophenyl)-derivatives,[1b,3] and by suggestions that spectroscopically undetected alkylpalladium(IV) species are formed as intermediates.[1b,4–7] In developing the chemistry of mono- and di-methylpalladium(II) complexes with nitrogen donor ligands we have noted that dimethyl[2,2-bis(pyrazol-1-yl)propane]palladium(II) reacts instantly and cleanly with iodomethane to form the palladium(II) complex, [$PdMe\{(pz)_2CMe_2\}I$].[8] However, extension of this reaction chemistry to 2,2′-bipyridyl (bpy) has led to isolation of *fac*-[$PdMe_3$(bpy)I] and the first *X*-ray structural analysis in organopalladium(IV) chemistry.

Dimethyl(2,2′-bipyridyl)palladium(II) has been described,[9] but may be more conveniently prepared in high yield† by the

† Yield >90%, does not require recrystallization.

method reported for analogous poly(pyrazol-1-yl)alkane complexes.[8] A saturated solution of orange [$PdMe_2$(bpy)] in acetone was treated with an excess of iodomethane at ambient temperature to give a colourless solution, and on evaporation to *ca.* 3/4 volume, colourless crystals of *fac*-trimethyl(2,2′-bipyridyl)iodopalladium(IV) were collected and dried under vacuum.‡

The *X*-ray structural study§ of *fac*-[$PdMe_3$(bpy)I] reveals an octahedral geometry for palladium with a *fac*-$PdMe_3$ group (Figure 1), as found in related triorganoplatinum(IV) chemistry.[1a,10–12] Some distortion from regular geometry results from the small 'bite' of 2,2′-bipyridyl, giving N(a1)–Pd–N(b1) 75.6(2)°, C(a)–Pd–N(b1) 97.4(3), and C(b)–Pd–N(a1) 100.1(3)°, with the remaining angles 86.6(3)—93.9(2)°. There are no reported structural studies of simple alkylpalladium(II) nitrogen donor complexes to allow a direct comparison of bond lengths in the two oxidation states. However, on comparison with the related platinum(IV) complex of bis-(3,5-dimethylpyrazol-1-yl)methane, *fac*-[$PtMe_3\{(Me_2pz)_2CH_2\}I$],[12] it is of interest that the complexes have similar M–C (within 3σ) and M–I [2.834(1)(Pd), 2.843(1) Å (Pt)] bond distances.

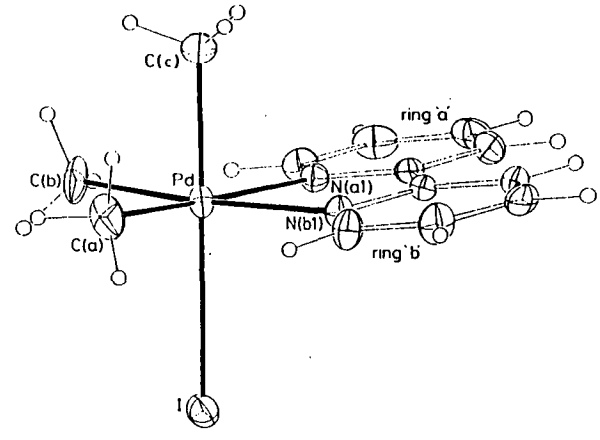

Figure 1. A molecular projection for *fac*-[$PdMe_3$(bpy)I] showing selected atom numbering; 20% thermal ellipsoids are shown for the non-hydrogen atoms, and hydrogen atoms (constrained at estimated idealized positions from difference map locations) have been given an arbitrary radius of 0.1 Å. Selected bond distances and angles: Pd–C(a,b,c) 2.046(7), 2.034(7), 2.040(6) Å, Pd–N(a1,b1) 2.188(5), 2.173(5) Å, Pd–I 2.834(1) Å, C(a)–Pd–C(b,c) 86.6(3), 87.0(3)°, C(b)–Pd–C(c) 86.8(3)°, C(a)–Pd–N(a1,b1) 172.3(3), 97.4(3)°, C(b)–Pd–N(a1,b1) 100.1(3), 174.2(3)°, C(c)–Pd–N(a1,b1) 89.5(2), 89.3(3)°, I–Pd–C(a,b,c) 93.9(2), 91.7(2), 178.1(2)°, I–Pd–N(a1,b1) 89.8(1), 92.1(1)°, N(a1)–Pd–N(b1) 75.6(2)°. The bpy system is substantially planar (χ^2 = 70) with deviations of Pd, C(a), and C(b) being 0.218, 0.496, and 0.556 Å, respectively.

‡ Dimethyl(2,2′-bipyridyl)platinum(II) reacts similarly.[10] The new complexes *fac*-[$PdMe_3$(bpy)I] (*ca.* 60% yield) and [PdMe(bpy)I] (*ca.* 90%) have satisfactory microanalyses (C, H, N, I) and ^{1}H n.m.r. spectra [$(CD_3)_2CO$, 300 MHz] that differ from each other and [$PdMe_2$(bpy)].

fac-[$PdMe_3$(bpy)I]: δ (Me_4Si) 8.95 [2H, ddd, H(6), ^3J(5,6) 5.27, ^4J(4,6) 1.66, ^5J(3,6) 0.78 Hz], 8.65 [2H, m, H(3), ^3J(3,4) 8.12, ^4J(3,5) *ca.* 1 Hz], 8.25 [2H, ddd, H(4), ^3J(3,4) 8.12, ^3J(4,5) 7.60, ^5J(4,6) 1.66 Hz], 7.80 [2H, ddd, H(5), ^3J(4,5) 7.60, ^3J(5,6) 5.27, ^4J(3,5) 1.17 Hz], 1.85 [6H, s, CH_3 (equatorial)], 1.14 [3H, s, CH_3(axial)].

[PdMe(bpy)I]: 9.53 [1H, ddd, $H(6)_{trans\text{-}I}$, ^3J(5,6) 5.31, ^4J(4,6) 1.73, ^5J(3,6) 0.84 Hz], 8.70 [1H, m, $H(6)_{trans\text{-}Me}$, ^3J(5,6) 5.56 Hz], 8.58 [1H, m, $H(3)_{trans\text{-}Me}$, ^3J(3,4) 8.08, ^4J(3,5) 1.40, ^5J(3,6) 0.82 Hz], 8.51 [1H, m, $H(3)_{trans\text{-}I}$, ^3J(3,4) 8.12, ^4J(3,5) *ca.* 1 Hz], 8.34 [1H, ddd, $H(4)_{trans\text{-}Me}$, ^3J(3,4) 8.08, ^3J(4,5) 7.56, ^4J(4,6) 1.60 Hz], 8.20 [1H, ddd, $H(4)_{trans\text{-}I}$, ^3J(3,4) 8.12, ^3J(4,5) 7.58, ^4J(4,6) 1.73 Hz], 7.85 [1H, ddd, $H(5)_{trans\text{-}Me}$, ^3J(4,5) 7.56, ^3J(5,6) 5.56, ^4J(3,5) 1.40 Hz], 7.70 [1H, ddd, $H(5)_{trans\text{-}I}$, ^3J(4,5) 7.58, ^3J(5,6) 5.31, ^4J(3,5) 1.20 Hz], 0.83 [3H, s, CH_3].

[$PdMe_2$(bpy)]: 8.87 [2H, ddd, H(6), ^3J(5,6) 5.26, ^4J(4,6) 1.64, ^5J(3,6) 0.78 Hz], 8.46 [2H, m, H(3), ^3J(3,4) 8.10, ^4J(3,5) *ca.* 1 Hz], 8.27 [2H, ddd, H(4), ^3J(3,4) 8.11, ^3J(4,5) 7.56, J(4,6) 1.70 Hz], 7.69 [2H, ddd, H(5), ^3J(4,5) 7.56, ^3J(5,6) 5.25, ^4J(3,5) 1.23 Hz], 0.24 [6H, s, CH_3].

§ *Crystal data:* $C_{13}H_{17}IN_2Pd$, M = 434.6, monoclinic, space group $P2_1/c$ (C_{2h}^5 No. 14), Z = 4, a = 7.917(4), b = 9.528(4), c = 20.207(8) Å, β = 104.28(4)°, U = 1477(1) Å^3, D_c = 1.95 g cm^{-3}, $F(000)$ = 832. The structure was determined using diffractometer data (Mo-K_α radiation, λ = 0.71069 Å) at 295 K, and refined to R 0.032 for 1822 'observed' reflections. Crystal size 0.10 × 0.25 × 0.08 mm.

A unique data set was measured at 295 K within the limit $2\theta_{max}$ = 50° using a Syntex $P2_1$ four-circle diffractometer in conventional 2θ/θ scan mode; 2619 independent reflections were measured, 1822 with $I > 3\sigma(I)$ being considered 'observed' and used in the full matrix least squares refinement after analytical absorption correction and solution of the structure by vector methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x,y,z)_H$ were constrained at estimates idealized from difference map locations, while U_{iso} (H) were estimated. Residuals (F) at convergence were R = 0.032, R' = 0.027 [statistical weights derived from $\sigma^2(I) = \sigma^2(I)_{diff} + 0.00005\sigma^4(I)_{diff}$]. Neutral complex scattering factors were used;[14] computation used the XTAL program system[15] implemented by S. R. Hall on a Perkin-Elmer computer.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

In $(CD_3)_2CO$ at 10 °C, the ^{1}H n.m.r. spectrum of the complex initially shows *fac*-[$PdMe_3$(bpy)I] only, but disappearance of resonances of the complex occurs over several hours with concurrent appearance of resonances arising from ethane and methyl(2,2′-bipyridyl)iodopalladium(II); at 25 °C this reductive elimination reaction requires 30—40 min for completion. The new complex [PdMe(bpy)I] may be synthesized independently, forming as yellow crystals on addition of bpy to an acetone solution of *trans*-[{$PdMe(SMe_2)(\mu\text{-}I)$}$_2$].[13] Both oxidative addition and reductive elimination may be monitored by n.m.r. spectroscopy, *e.g.* on addition of iodomethane in $(CD_3)_2CO$ to [$PdMe_2$(bpy)] in $(CD_3)_2CO$ to give a 1 : 1 mol ratio of reactants, spectra show *immediate* complete conversion into *fac*-[$PdMe_3$(bpy)I] followed by subsequent slow formation of ethane and [PdMe(bpy)I].

Solid *fac*-[$PdMe_3$(bpy)I] also reductively eliminates ethane, with violent conversion into a yellow solid at 100—110 °C and subsequent melting at 212—214 °C (decomp.), the melting point of [PdMe(bpy)I]. However, the complex is stable when stored at −20 °C, and becomes pale yellow over several days at ambient temperature.

The results reported here support earlier suggestions that transient alkylpalladium(IV) species occur as intermediates,[4–7] in particular in coupling reactions catalysed by palladium substrates.[6] The oxidative addition–reductive elimination reactivity, and the stability of neutral *fac*-[$PdMe_3$(bpy)I] at temperatures near ambient, suggest that development of a rich organometallic chemistry of palladium(IV) may be possible.

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References

1 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, New York, 1982, vol. 6, (a) F. R. Hartley, pp. 587—588; (b) P. M. Maitlis, P. Espinet, and M. J. H. Russell, pp. 339—340.
2 W. J. Pope and S. J. Peachey, *Proc. Chem. Soc.*, 1907, **23**, 86; *J. Chem. Soc.*, 1909, 571.
3 R. Uson, J. Fornies, and R. Navarro, *Synth. React. Inorg. Metal-Org. Chem.*, 1977, **7**, 235; *J. Organomet. Chem.*, 1975, **96**, 307.
4 T. Ito, H. Tsuchiya, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 1319.
5 J. K. Stille and K. S. Y. Lau, *J. Am. Chem. Soc.*, 1976, **98**, 5841; D. Milstein and J. K. Stille, *ibid.*, 1979, **101**, 4981.
6 A. Gillie and J. K. Stille, *J. Am. Chem. Soc.*, 1980, **102**, 4933; A. Moravskiy and J. K. Stille, *ibid.*, 1981, **103**, 4182.
7 P. Diversi, D. Fasce, and R. Santini, *J. Organomet. Chem.*, 1984, **269**, 285.
8 P. K. Byers and A. J. Canty, *Inorg. Chim. Acta*, 1985, **104**, L13.
9 G. Calvin and G. E. Coates, *J. Chem. Soc.*, 1060, 2008.
10 J. Kuyper, R. van der Laan, F. Jeanneaus, and K. Vrieze, *Transition Met. Chem.*, 1976, **1**, 199; J. K. Jawad and R. J. Puddephatt, *J. Chem. Soc., Dalton Trans.*, 1977, 1466.
11 D. E. Clegg, J. R. Hall, and G. A. Swile, *J. Organomet. Chem.*, 1972, **38**, 403.
12 H. C. Clark, G. Ferguson, V. K. Jain, and M. Parvez, *J. Organomet. Chem.*, 1984, **270**, 365.
13 P. K. Byers, and A. J. Canty, L. M. Engelhardt, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1986, 1731.
14 'International Tables for *X*-Ray Crystallography,' eds. J. A. Ibers and W. C. Hamilton, Kynoch Press, Birmingham, 1974, vol. 4.
15 'The XTAL System,' eds. J. M. Stewart and S. R. Hall, Technical Report TR-1364, Computer Science Center, University of Maryland, 1983.

Synthesis of the First Organopalladium(IV) Cations, including the First *X*-Ray Study of Isostructural Organopalladium(IV) and Platinum(IV) Complexes, [*fac*-MMe_3{tris(pyrazol-1-yl)methane-*N*,*N*',*N*''}]I

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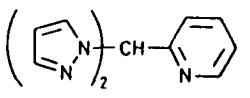
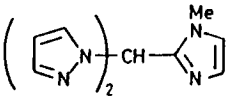
Stable organopalladium(IV) complexes [*fac*-$PdMe_3$(L)]I (L = tridentate nitrogen donor ligand) are formed on oxidative addition of iodomethane to $PdMe_2$(L); the tris(pyrazol-1-yl)methane complex is isostructural with the platinum(IV) analogue.

Organoplatinum(IV) chemistry has been extensively developed since the initial report of $[PtMe_3(\mu_3\text{-}I)]_4$ and related compounds in 1907,[1,2] and although palladium has a well established role in organic synthesis and catalysis,[3] the organometallic chemistry of palladium(IV) is limited. The main reports are suggestions that organopalladium(IV) species are formed as intermediates in some reactions and catalytic processes,[2,4—9] and the isolation of several neutral pentafluorophenyl complexes[10] and a single hydrocarbyl complex, *fac*-[$PdMe_3$(2,2'-bipyridyl)I].[11] This complex, obtained by oxidative addition of iodomethane to the palladium(II) complex $PdMe_2$(bpy) (bpy = 2,2'-bipyridine), reductively eliminates ethane in solution to form PdMe(bpy)I, and is the only



$(pz)_2(py)CH$



$(pz)_2(mim)CH$

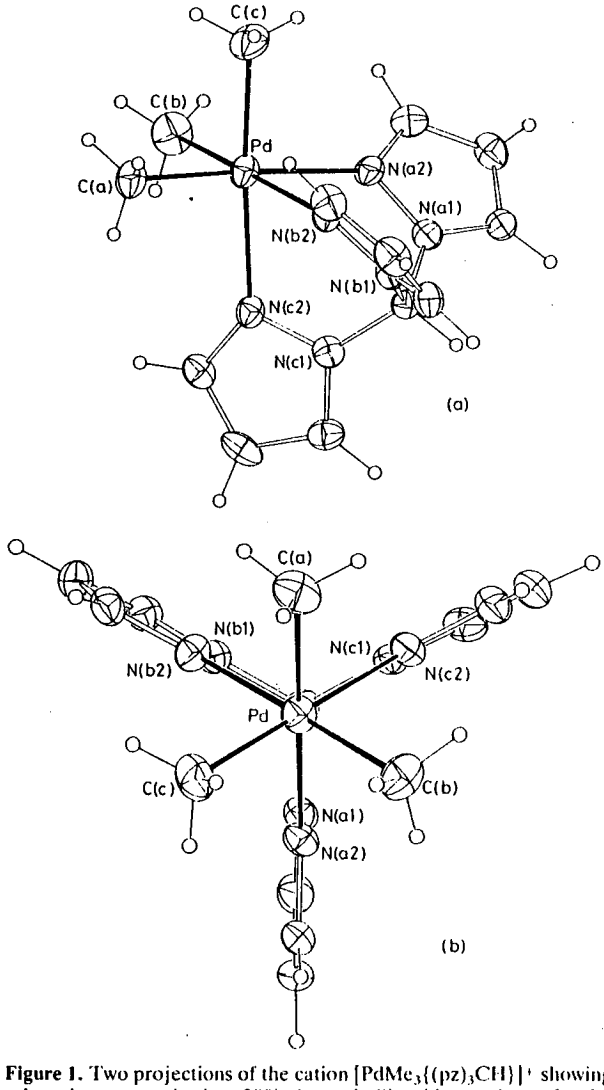


Figure 1. Two projections of the cation $[PdMe_3\{(pz)_3CH\}]^+$ showing selected atom numbering; 20% thermal ellipsoids are shown for the non-hydrogen atoms, and hydrogen atoms (constrained at estimated idealized positions) have been given an arbitrary radius of 0.1 Å. Projection (b) is a view directly along the (non-crystallographic) three-fold axis. Selected bond distances (Å) and angles (°) for the isostructural palladium and platinum complexes, with values for platinum given in brackets []: M–C(a) 2.036(11) [2.031(8)], M–C(b) 2.060(9) [2.056(7)], M–C(c) 2.049(10) [2.056(7)], M–N(a2) 2.191(8) [2.156(6)], M–N(b2) 2.207(7) [2.156(5)], M–N(c2) 2.225(7) [2.189(5)] Å, C(a)–M–C(b) 86.6(4) [87.9(3)], C(a)–M–C(c) 88.0(4) [89.2(3)], C(b)–M–C(c) 87.4(4) [88.4(3)], N(a2)–M–N(b2) 83.2(3) [84.1(2)], N(a2)–M–N(c2) 81.7(3) [82.9(2)], N(b2)–M–N(c2) 82.4(2) [83.7(2)], C(a)–M–N(a2) 176.8(3) [177.3(2)], C(a)–M–N(b2) 95.1(3) [94.4(2)], C(a)–M–N(c2) 95.4(3) [94.6(2)], C(b)–M–N(a2) 95.0(3) [93.5(3)], C(b)–M–N(b2) 177.8(3) [176.9(3)], C(b)–M–N(c2) 96.1(3) [94.0(2)], C(c)–M–N(a2) 94.8(3) [93.2(3)], C(c)–M–N(b2) 94.1(3) [93.8(2)], C(c)–M–N(c2) 175.3(3) [175.6(3)]°.

organopalladium(IV) complex characterised by *X*-ray crystallography.[11] We report here the synthesis of organopalladium(IV) cations which are stable at ambient temperature, and a crystallographic study of isostructural palladium(IV) and platinum(IV) organometallic compounds.

The tris(pyrazol-1-yl)methane complex $PdMe_2\{(pz)_3CH\}$ reacts readily with iodomethane in acetone at ambient temperature to give immediately crystals of $[PdMe_3\{(pz)_3CH\}]I$.† A series of complexes involving tripodal nitrogen donor ligands‡ containing pyrazol-1-yl (pz), pyridin-2-yl (py), and *N*-methylimidazol-2-yl (mim) groups were also readily obtained, $[PdMe_3(L)]I$ [L = $(pz)_2(py)CH$, $(pz)_2(mim)CH$, and $(py)_3CH$]. The palladium(II) precursors, $PdMe_2(L)$, were synthesized in a manner similar to that reported earlier for $PdMe_2\{(pz)_3CH\}$.[14]

Crystals of $[MMe_3\{(pz)_3CH\}]I$ (M = Pd, Pt§) are isomorphous,¶ and the isostructural cations have octahedral *'fac-*

† The complexes $[PdMe_3(L)]I$ [L = $(pz)_2(py)CH$, $(pz)_2(mim)CH$, $(py)_3CH$], and $[MMe_3\{(pz)_3CH\}]I$ (M = Pd, Pt) have satisfactory microanalyses (C, H, N) and ^1H n.m.r. spectra ($CDCl_3$, 300 MHz). N.m.r. spectra for $[PdMe_3(L)]I$ are different from their $PdMe_2(L)$ and $PdMe(L)I$ analogues.

$[PtMe_3\{(pz)_3CH\}]I$: δ (Me_4Si) 12.24 [1H, s, CH], 9.08 [3H, dd, 5-H, $^3J(4,5)$ 2.7, $^4J(3,5)$ 0.6 Hz], 7.73 [3H, d, 3-H, $^3J(3,4)$ 2.1 Hz], 6.54 [3H, dd, 4-H, $^3J(4,5)$ 2.7, $^3J(3,4)$ 2.1 Hz], 1.14 [9H, pseudo t, Me, $^2J(^1H–^{195}Pt)$ 72 Hz].

$[PdMe_3\{(pz)_3CH\}]I$: 12.02 [1H, s, CH], 8.99 [3H, dd, 5-H, $^3J(4,5)$ 2.7, $^4J(3,5)$ 0.6 Hz], 7.70 [3H, d, 3-H, $^3J(3,4)$ *ca.* 1.8 Hz], 6.47 [3H, dd, 4-H, $^3J(4,5)$ 2.7, $^3J(3,4)$ *ca.* 2 Hz], 1.58 [9H, s, Me].

$[PdMe_3\{(pz)_2(py)CH\}]I$: 10.73 [1H, s, CH], 9.01 [2H, d, 5-H (pz), $^3J(4,5)$ 2.7 Hz], 8.87 [1H, d, 6-H (py), $^3J(5,6)$ 7.8 Hz], 8.56 [1H, d, 3-H (py), $^3J(3,4)$ 5.4 Hz], 8.06 [1H, ddd, 5-H (py), $^3J(5,6)$ 7.8, $^4J(4,5)$ 7.8, $^5J(3,5)$ 1.8 Hz], *ca.* 7.6 [3H, m, 3-H (pz) and 4-H (py)], 6.43 [2H, dd, 4-H (pz), $^3J(4,5)$ 2.6, $^3J(3,4)$ *ca.* 1.9 Hz], 1.59 [3H, s, Me *trans*-py], 1.53 [6H, s, Me *trans*-pz].

$[PdMe_3\{(pz)_2(mim)CH\}]I$: 10.60 [1H, s, CH], 9.24 [2H, dd, 5-H (pz), $^3J(4,5)$ 2.7, $^4J(3,5)$ 0.6 Hz], 7.62 [2H, d, 3-H (pz), $^3J(3,4)$ 1.8 Hz], 7.15 [1H, d, 5-H (mim), $^3J(4,5)$ 1.5 Hz], 7.00 [1H, d, 4-H (mim), $^3J(4,5)$ 1.5 Hz], 6.39 [2H, dd, 4-H (pz), $^3J(4,5)$ 2.7, $^3J(3,4)$ 1.7 Hz], 4.36 [3H, s, NMe], 1.56 [6H, s, Me *trans*-pz], 1.38 [3H, s, Me *trans*-mim].

$[PdMe_3\{(py)_3CH\}]I$: 8.93 [3H, d, 6-H, $^3J(5,6)$ 7.7 Hz], 8.47 [3H, dd, 3-H, $^3J(3,4)$ 5.6, $^4J(3,5)$ 1.7 Hz], 8.27 [1H, s, CH], 7.96 [3H, ddd, 5-H, $^3J(5,6)$ 7.7, $^4J(4,5)$ 7.7, $^5J(3,5)$ 1.7 Hz], 7.45 [3H, ddd, 4-H, $^3J(4,5)$ 7.7, $^3J(3,4)$ 5.6, $^4J(4,6)$ 1.3 Hz], 1.50 [9H, s, Me].

‡ The new ligands (pyridin-2-yl)bis(pyrazol-1-yl)methane $[(pz)_2(py)CH]$[12] and (*N*-methylimidazol-2-yl)bis(pyrazol-1-yl)-methane $[(pz)_2(mim)CH]$ were obtained on condensation of bis(pyrazol-1-yl) ketone with pyridine-2-carbaldehyde and *N*-methylimidazole-2-carbaldehyde, respectively, with the former synthesis employing cobalt(II) chloride catalysis following the reported procedure for synthesis of related bis(pyrazol-1-yl)alkanes.[13]

§ The platinum(IV) complex, $[PtMe_3\{(pz)_3CH\}]I$, was obtained directly from $[PtMe_3(\mu_3\text{-}I)]_4$ and $(pz)_3CH$ in acetone. In contrast to the reactivity observed for $PdMe\{(pz)_3CH\}$, $PtMe_2\{(pz)_3CH\}$ reacts with MeI in acetone to form a Pt(IV) complex containing cyclometallated $(pz)_3CH$, $[PtMe_2\{(pz)_2(C_3H_2N_2)CH\text{-}N,N,C^5\}I]$.[12] The complex has spectra similar to that reported for its pyridine derivative $[PtMe_2\{(pz)_2(C_3H_2N_2)CH\text{-}N,N,C^5\}(py)]I$, formed on oxidative addition of MeI to $[PtMe\{(pz)_2(C_3H_2N_2)CH\text{-}N,C^5\}(py)]$,[15] and the new complex is assumed to be formed similarly *via* cyclometallation of $PtMe_2\{(pz)_3CH\}$.

¶ *Crystal data:* Crystals of the palladium complex obtained from its preparation were suitable for *X*-ray studies, and crystals of the platinum complex were obtained from an acetone solution exposed to diethyl ether vapour in a sealed chamber at *ca.* −20 °C. The complexes $[MMe_3\{(pz)_3CH\}]I$ (M = Pd, Pt) are monoclinic, space group *C*2/*c*, with *Z* = 8. Palladium [platinum] complex cells, determined on the same instrument on the same day are *a* = 21.254(8) [21.253(8)], *b* = 9.213(5) [9.099(4)], *c* = 19.144(8) [19.284(8)] Å, β = 105.65(3) [105.63(3)]°, D_c = 1.81[2.15] g cm^{-3}, *F*(000) = 1904[2160]. The structures were determined using diffractometer data (Mo-K_α radiation, λ = 0.7106$_9$ Å) at 295 K, and refined to *R* 0.040 (Pd), 0.031 (Pt) for 2030 (Pd), 3284 (Pt) 'observed' $I > 3\sigma I$ absorption corrected reflections μ(Mo-K_α) = 25[91] cm^{-1} (full-matrix least squares; anisotropic thermal parameters for the non-hydrogen atoms). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

MC_3N_3' geometry (Figure 1), with analogous angles at Pd and Pt within *ca.* 2°. The complexes have C–M–C angles 86.6(4)—88.0(4) (Pd) and 87.9(3)—89.2(3)° (Pt), with smaller N–M–N angles owing to the 'bite' of tridentate $(pz)_3CH$, 81.7(3)—83.2(3) (Pd) and 82.9(2)—84.1(2)° (Pt). The M–C distances are identical in the complexes, 2.04_8 (Pd) and 2.04_8 Å (Pt), but there is an appreciable difference in M–N distances, with that for the palladium complex being appreciably longer than that for platinum, 2.20_8 and 2.16_7 Å respectively; *cf.* the difference reported for metal–phosphorus bond lengths in the isostructural M(II) complexes *cis*-$MMe_2(PPh_2Me)_2$ (M = Pd, Pt), where the more precise M–P bond length determinations give Pd–P *ca.* 0.039(1) Å longer than Pt–P.[16] In these complexes, Pd–C distances were appreciably shorter than Pt–C distances by 0.030(4) Å.[16]

The palladium(IV) complexes exhibit ^1H n.m.r. spectra in $CDCl_3$ which are consistent with the presence of cations [*fac*-$PdMe_3(L\text{-}N,N',N'')]^+$ with tridentate L, as in the solid state for the $(pz)_3CH$ complex, rather than neutral [$PdMe_3$-(L-*N*,*N'*)I] with bidentate L; *e.g.* spectra of [$PdMe_3(L)$]I [L = $(pz)_3CH$, $(py)_3CH$] exhibit a single methyl and donor ring environment, and the spectrum of [$PdMe_3\{(pz)_2(py)CH\}$]I exhibits two methyl environments, in a 2 : 1 ratio, and single pyrazole and pyridine environments, in a 2 : 1 ratio. The platinum(IV) compiex, [$PtMe_3\{(pz)_3CH\}$]I, has a spectrum similar to that reported for the hexafluorophosphate salt,[17] and similar to that for [$PdMe_3\{(pz)_3CH\}$]I with the addition of $^2J(^1H\text{–}^{195}Pt)$ satellites. The ligand methine protons for the complexes [$PdMe_3(L)$]I [L = $(pz)_3CH$, $(pz)_2(py)CH$, and $(pz)_2(mim)CH$] exchange with the deuterium of $CDCl_3$, over several hours, and the exchange may be reversed on addition of $CHCl_3$ to the solid obtained on removal of $CDCl_3$–$CHCl_3$.

The 2,2'-bipyridyl complex, *fac*-[$PdMe_3(bpy)$I] requires storage at < *ca.* −20 °C,[11] and reductively eliminates ethane to form PdMe(bpy)I in $CDCl_3$, with complete reaction after *ca.* 30—40 min at ambient temperature. In contrast, for [$PdMe_3(L)$]I in $CDCl_3$, only the $(pz)_3CH$ complex gave trace amounts of ethane and PdMe$\{(pz)_3CH\}$I‖ after *ca.* 2—4 h, indicating that development of a wide range of stable organometallic compounds of palladium(IV) may be possible.

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‖ Prepared as reported,[14] or more conveniently on reaction of *trans*-$[\{PdMe(SMe_2)(\mu\text{-}I)\}_2]$[18] with $(pz)_3CH$ in acetone.

References

1 W. J. Pope and S. J. Peachey, *Proc. Chem. Soc.*, 1907, **23**, 86; *J. Chem. Soc.*, 1909, 571.
2 P. M. Maitlis, P. Espinet, and M. J. H. Russell, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, New York, 1982, vol. 6, pp. 339—340.
3 *e.g.*, R. F. Heck, 'Palladium Reagents in Organic Syntheses,' Academic Press, London, 1985; B. M. Trost, in ref. 2, vol. 8, pp. 799—938.
4 P. M. Maitlis, 'The Organic Chemistry of Palladium,' Academic Press, 1971, vol. 1, pp. 83—84.
5 P. M. Henry, *Adv. Organomet. Chem.*, 1975, **13**, 363.
6 T. Ito, H. Tsuchiya, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 1319; F. Ozawa, K. Kurihara, T. Yamamoto, and A. Yamamoto, *ibid.*, 1985, **58**, 399.
7 J. K. Stille and K. S. Y. Lau, *J. Am. Chem. Soc.*, 1976, **98**, 5841; D. Milstein and J. K. Stille, *ibid.*, 1979, **101**, 4981, 4992; A. Gillie and J. K. Stille, *ibid.*, 1980, **102**, 4933; M. K. Loar and J. K. Stille, *ibid.*, 1981, **103**, 4174; A. Moravskiy and J. K. Stille, *ibid.*, 1981, **103**, 4182.
8 P. Diversi, D. Fasce, and R. Santini, *J. Organomet. Chem.*, 1984, **269**, 285.
9 H. Kurosawa, M. Emoto, and A. Urabe, *J. Chem. Soc., Chem. Commun.*, 1984, 968.
10 R. Usón, J. Forniés, and R. Navarro, *Synth. React. Inorg. Met.-Org. Chem.*, 1977, **7**, 235; *J. Organomet. Chem.*, 1975, **96**, 307.
11 P. K. Byers, A. J. Canty, B. W. Skelton, and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1986, 1722.
12 A. J. Canty and R. T. Honeyman, unpublished results.
13 K. I. Thé and L. K. Peterson, *Can. J. Chem.*, 1973, **51**, 422.
14 P. K. Byers and A. J. Canty, *Inorg. Chim. Acta*, 1985, **104**, L13.
15 A. J. Canty, R. T. Honeyman, B. W. Skelton, and A. H. White, *Inorg. Chim. Acta*, 1986, **114**, L39.
16 J. M. Wisner, T. J. Bartczak, and J. A. Ibers, *Organometallics*, 1986, **5**, 2044.
17 H. C. Clark, G. Ferguson, V. K. Jain, and M. Parvez, *J. Organomet. Chem.*, 1984, **270**, 365.
18 P. K. Byers, A. J. Canty, L. M. Engelhardt, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1986, 1731.

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Preliminary communication

Convenient synthetic routes to $MePd^{II}$, Me_2Pd^{II}, and Me_3Pd^{IV} complexes. The crystal structure of the $MePd^{II}$ complex [MePd(2,2′-bipyridyl)(γ-picoline)]BF_4

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Abstract

The pyridazine complex $[Me_2Pd(pyd)]_n$, stable as a solid on storage at ca. −20 °C and obtained on reaction of *trans*-$PdCl_2(SMe_2)_2$ with methyllithium and pyridazine at low temperature, is an excellent precursor for the synthesis of Me_2Pd^{II} and Me_3Pd^{IV} complexes under mild conditions, in particular for ligands sensitive to MeLi. Similarly, $[MePd(SMe_2)(\mu\text{-}I)]_2$ is a suitable precursor for the synthesis of neutral and cationic $MePd^{II}$ complexes, including [MePd(2,2′-bipyridyl)(γ-picoline)]BF_4, which has been characterized by X-ray crystallography.

Dialkylpalladium(II) complexes of nitrogen donor ligands are usually synthesized from alkyllithium reagents [1–6], either by reaction of the reagent with the dihalopalladium(II) complex [1–3], or by addition of ligand to a solution obtained on reaction of *trans*-$PdCl_2(SMe_2)_2$ with MeLi [4–6], although $\overline{CH_2CH_2CH_2CH_2}$Pd(bipy) has been obtained by reaction of 2,2′-bipyridyl with the tetramethylethylenediamine (tmen) complex [2] and Et_2Pd(bipy) by reaction of $Et_2Al(OEt)$ with $Pd(acac)_2$ in the presence of bipy [7]. These routes require the ligand to be unreactive toward alkyllithium or alkylaluminium reagents [1–7], prior synthesis and characterization of dihalo complexes [1–3], or the use of donor ligands of sufficient basicity to displace bidentate tmen [2].

Pyridazine was chosen as a ligand in view of its low basicity, and we have found that $[Me_2Pd(pyd)]_n$ is a suitable precursor for direct synthesis of Me_2Pd^{II} and Me_3Pd^{IV} complexes containing ligands sensitive to MeLi. We have also demonstrated the convenient application of $[MePd(SMe_2)(\mu\text{-}I)]_2$ for the synthesis of

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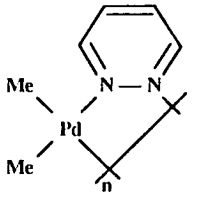

$[Me_2Pd(pyd)]_n$

$MePd^{II}$ complexes, including the γ-picoline complex $[MePd(bipy)(\gamma\text{-pic})]^+$ which has been characterized by X-ray crystallography.

The pyridazine complex was obtained by addition of 2.05 mole equivalents of halide-free methyllithium to *trans*-$PdCl_2(SMe_2)_2$ in diethyl ether (e.g. 1.5 g in ca. 130 ml) at ca. −60 °C under nitrogen, followed by addition of an ether solution of pyridazine at ca. −40 °C, hydrolysis at ca. −15 °C, and rapid filtration. The yellow-orange solid (70–80% yield) was washed with water and several portions of anhydrous ether, dried immediately under high vacuum at ambient temperature, and stored at ca. −20 °C. The complex exhibits a simple ^1H NMR spectrum in $(CD_3)_2CO$, consistent with the formulation $[Me_2Pd(pyd)]_n$ (Table 1), but decomposition takes place in solution during 10–15 minutes. Low stability prevented the determination of the value of *n* by osmometry in organic solvents.

The pyridazine complex reacts immediately and cleanly with PPh_3 in acetone at ambient temperature to give *cis*-$Me_2Pd(PPh_3)_2$ (55% yield on isolation, purification not necessary), illustrating its application in synthesis of phosphine complexes, and with bidentate nitrogen donor ligands containing ketone and alkene groups sensitive to MeLi to give $Me_2Pd(L)$ {L = (py)(mim)C=O, $(mim)_2C$=O, and (py)(mim)C=CH_2, where py = pyridin-2-yl and mim = *N*-methylimidazol-2-yl} (Table 1). The ligand (py)(mim)C=CH_2 is shown in Fig. 1.

Reports of hydrocarbylpalladium(IV) complexes are limited to a single neutral complex, *fac*-$Me_3Pd(bipy)I$, and four ionic complexes, [*fac*-$Me_3Pd(L')]I$ (L′ = $(pz)_3CH$, $(pz)_2(py)CH$, $(pz)_2(mim)CH$, and $(py)_3CH$, where pz = pyrazol-1-yl), obtained on oxidative addition of iodomethane to the appropriate Me_2Pd^{II} complexes [5,6]. The complexes, and the new complex $Me_3Pd(phen)I$, may be isolated in ca. 45–67% yield directly from $[Me_2Pd(pyd)]_n$ on reaction with bipy, phen · H_2O, or L′ followed by MeI in acetone at 0 °C, so avoiding the need for prior synthesis and characterization of Me_2Pd^{II} complexes of the ligands; solutions of complexes *fac*-$Me_3Pd(L)I$ where L contain ketone or alkene groups were obtained similarly, or from $Me_2Pd(L)$ (e.g. Fig. 1), but isolation could not be effected before reductive elimination of ethane to form MePd(L)I had occurred.

Monoalkylpalladium(II) complexes of nitrogen donor ligands have been obtained by reaction of $(Me_3CCH_2)_2Pd(bipy)$ with benzyl bromide to give Me_3CCH_2Pd-(bipy)Br [3], reaction of MeMgI and the ligand with *trans*-$PdCl_2(SMe_2)_2$ at low temperature [4], reaction of $[MePd(SMe_2)I]_2$ [8] with the ligand for the synthesis of MePd(bipy)I and MePd(L′)I [5,6], and reaction of $[MePd(SMe_2)Cl]_2$ [8] with 2,9-dimethyl-1,10-phenanthroline for the synthesis of MePd(Me_2phen)Cl [9]. We report here the utility of $[MePd(SMe_2)I]_2$ (obtained in 91% yield from *trans*-$PdCl_2(SMe_2)_2$ [8]) for the synthesis, at ambient temperature, of other classes of $MePd^{II}$ complexes, including a series of crystalline cationic complexes (Table 1).

Table 1

Yield and characterization data for complexes isolated [a]

Complex	Colour	Yield	^{1}H NMR	
			δ(MePd)	Solvent
Dimethylpalladium(II) complexes				
$[Me_2Pd(pyd)]_n$	yellow-orange	75	0.06	$(CD_3)_2CO$
cis-$Me_2Pd(PPh_3)_2$ [b]	white	55	0.20	$CDCl_3$
$Me_2Pd(bipy)$ [c]	yellow-orange	82	0.24	$(CD_3)_2CO$
$Me_2Pd\{(py)(mim)C{=}O\}$	yellow-orange	46	0.08, −0.06	$(CD_3)_2CO$
$Me_2Pd\{(mim)_2C{=}O\}$	orange	78	0.10	$(CD_3)_2CO$
$Me_2Pd\{(py)(mim)C{=}CH_2\}$	yellow	52	0.08, −0.10	$(CD_3)_2CO$
Methylpalladium(II) complexes				
trans-$MePd(PPh_3)_2Cl$ [d]	white	75	−0.03	$CDCl_3$
MePd(bipy)Cl [e]	pale yellow	73	1.04	$CDCl_3$
$MePd\{(pz)_2CMe_2\}Cl$	pale yellow	57	1.04	$CDCl_3$
trans-$MePd(PPh_3)_2Br$ [d]	yellow	79	0.08	$CDCl_3$
MePd(bipy)Br	yellow-orange	75	1.04	$CDCl_3$
$MePd\{(pz)_2CMe_2\}Br$	yellow	66	1.03	$CDCl_3$
trans-$MePd(PPh_3)_2I$ [b]	white	82	0.23	$CDCl_3$
MePd(bipy)I [i]	yellow	79	0.97	$CDCl_3$
$MePd\{(pz)_2CMe_2\}I$	yellow	73	0.98	$CDCl_3$
$MePd\{(py)(mim)C{=}O\}I$ [f]	yellow-orange	68	0.82	$(CD_3)_2CO$
$MePd\{(mim)_2C{=}O\}I$	yellow	88	0.77	$(CD_3)_2SO$
$MePd\{(py)(mim)C{=}CH_2\}I$ [g]	pale yellow	66	0.77	$(CD_3)_2CO$
[MePd(terpy)]I	orange	87	1.09	CD_3OD/ $(CD_3)_2SO$
$[MePd(bipy)(\gamma\text{-pic})]BF_4$	white	65	0.90	$(CD_3)_2CO$
$[MePd(bipy)(NCMe)]BF_4$	white	76	1.18	$(CD_3)_2CO$
$[MePd(bipy)(SMe_2)]BF_4$	white	63	1.00	$(CD_3)_2CO$
Trimethylpalladium(IV) complexes				
fac-$Me_3Pd(phen)I$	white	52	1.96, 1.20	$(CD_3)_2CO$
fac-$Me_3Pd(bipy)I$ and $[fac\text{-}Me_3Pd(L')]I$ [h]				

[a] All isolated new complexes have satisfactory ^{1}H NMR spectra, and microanalysis (C,H,N) except for $[Me_2Pd(pyd)]_n$ which is insufficiently stable at ambient temperature for postage for microanalysis. Previously reported complexes have ^{1}H NMR spectra in agreement with those reported [5,6,10,11]. [b] Previously reported [10]. [c] Previously reported [1,5]. [d] Previously reported [11]. [e] Previously reported, but synthetic method not given [12]. [f] ~ 90% Isomer with Me *trans* to mim, the other isomer has δ(MePd) 0.64. [g] ~ 93% Isomer with Me *trans* to mim, the other isomer has δ(MePd) 0.53. [h] All white, yield 45–67%, characterization data as reported earlier for preparation by a different route, bipy [5], and L′ = $(pz)_3CH$, $(pz)_2(py)CH$, $(pz)_2(mim)CH$, $(py)_3CH$ [6]. [i] Previously reported [5].

Neutral phosphine complexes are readily obtained, exemplified by isolation of *trans*-$MePd(PPh_3)_2I$ in 82% yield from acetone, and complexes of bidentate nitrogen donor ligands sensitive to MeLi are similarly obtained, e.g. $MePd\{(py)(mim)C{=}O\}I$. The complex $[MePd(SMe_2)I]_2$ is also a suitable precursor for the synthesis of bromo and chloro complexes. Thus, treatment of an acetonitrile solution with 2.4 mole equivalents of $AgNO_3$, followed by filtration to remove AgI, addition of 4.0 mole equivalents of KBr in a small volume of acetone/water with subsequent removal of the remaining Ag^+ as AgBr, and addition of L″ [bipy, $(pz)_2CMe_2$] or PPh_3 gave MePd(L″)Br or *trans*-$MePd(PPh_3)_2Br$. A similar proce-

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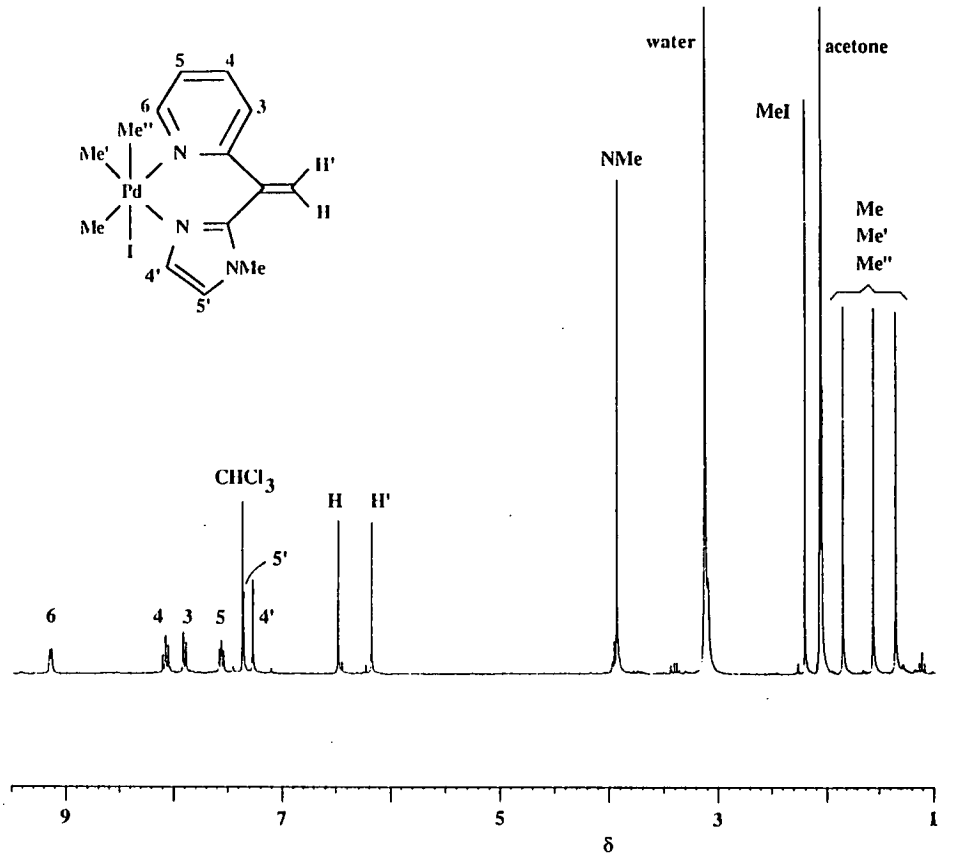

Fig. 1. The ^{1}H NMR spectrum of *fac*-$Me_3Pd\{(py)(mim)C{=}CH_2\}I$, obtained on addition of MeI to $Me_3Pd(py)(mim)C{=}CH_2\}$ in $(CD_3)_2CO$ at 0°C. Integration is appropriate for the assignments given, and H and H′ were assigned using long range enhanced correlation spectroscopy. Similar spectra, but with addition of free pyridazine resonances, are obtained on addition of $(py)(mim)C{=}CH_2$ to $[Me_2Pd(pyd)]_n$ followed by MeI.

dure, but with the addition of ligand preceded by addition of water and additional KCl with stirring for 15 min, gave the chloro analogues.

The ionic complexes, [MePd(terpy)]I and $[MePd(bipy)(\gamma\text{-pic})]BF_4$, are obtained on addition of 2,2′:6′,2″-terpyridyl to $[MePd(SMe_2)I]_2$ in acetone, or addition of bipy followed by $AgBF_4/\gamma$-picoline with subsequent filtration to remove AgI followed by crystallization of $[MePd(bipy)(\gamma\text{-pic})]BF_4$. An attempted preparation of $[MePd(bipy)(NCMe)]BF_4$, by this procedure gave $[MePd(bipy)(SMe_2)]BF_4$, but the acetonitrile complex may be readily isolated on treatment of MePd(bipy)I with $AgBF_4$/NCMe and filtration to remove AgI.

Crystals of the γ-picoline complex suitable for a structural study were obtained by dissolution of the complex in acetone, assisted by the minimum quantity of dichloromethane, followed by exposure to diethyl ether vapour in a sealed chamber at ambient temperature. Crystals of $[MePd(bipy)(\gamma\text{-pic})]BF_4$, $C_{17}H_{18}BF_4N_3Pd$, M = 457.6, are monoclinic, space group $P2_1/n$ with a 8.243(2), b 12.632(4), c 17.550(5) Å, β 95.75(2)°, U 1818.2(8) Å^3, D_c 1.67 g cm^{-3}, and $Z = 4$. 3216 Independent data

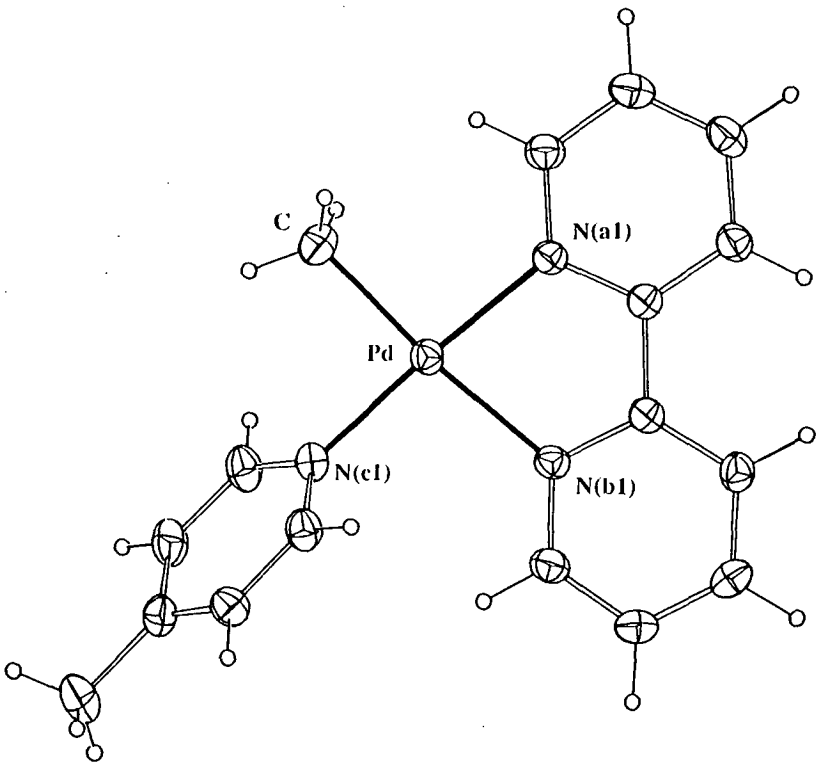

Fig. 2. The cation $[MePd(bipy)(\gamma\text{-pic})]^+$ projected normal to the '$PdCN_3$' coordination plane; 20% thermal ellipsoids are shown for the non-hydrogen atoms, and hydrogen atoms (constrained at estimated idealized positions) have been given an arbitrary radius of 0.1 Å. Selected bond distances and angles: Pd–C 2.036(6), Pd–N(a1,b1,c1) 2.049(4), 2.131(4), 2.033(4) Å, C–Pd–N(a1,b1,c1) 95.4(2), 174.3(2), 88.1(2)°, N(a1)–Pd–N(b1,c1) 79.1(2), 176.4(2)°, N(b1)–Pd–N(c1) 97.4(2)°.

were measured with a Syntex $P2_1$ four-circle diffractometer in conventional $2\theta/\theta$ scan mode ($2\theta_{max}$ 50°) with Mo-K_α (0.7106_9) Å) radiation. Full matrix least squares refinement converged at R and R' of 0.039 and 0.041 for the 2368 absorption corrected reflections having $I > 3\sigma(I)$ *.

The $[MePd(bipy)(\gamma\text{-pic})]^+$ cation, shown in Fig. 2, has square planar geometry for palladium, with bipy forming the smallest bond angle (N(a1)–Pd–N(b1) 79.1(2)°) and the carbon atom exhibiting the largest deviation from the 'CN_3' weighted mean plane (0.037 Å); the γ-picoline group forms a dihedral angle of 62.1° with the 'CN_3' mean plane.

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* The atomic coordinates, bond lengths and angles, and thermal parameters are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

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References and notes

1 G. Calvin and G.E. Coates, J. Chem. Soc., (1960) 2008.
2 P. Diversi, G. Ingrosso, A. Lucherini, and S. Murtas, J. Chem. Soc. Dalton Trans., (1980) 1633.
3 P. Diversi, D. Fasce, and R. Santini, J. Organomet. Chem., 269 (1984) 285.
4 P.K. Byers and A.J. Canty, Inorg. Chim. Acta, 104 (1985) L13.
5 P.K. Byers, A.J. Canty, B.W. Skelton, and A.H. White, J. Chem. Soc. Chem. Commun., (1986) 1722.
6 P.K. Byers, A.J. Canty, B.W. Skelton, and A.H. White, J. Chem. Soc. Chem. Commun., (1987) 1093.
7 R. Sustmann and J. Lau, Chem. Ber., 119 (1986) 2531.
8 P.K. Byers, A.J. Canty, L.M. Engelhardt, and A.H. White, J. Chem. Soc. Dalton Trans., (1986) 1731.
9 A. De Renzi, G. Morelli, A. Panunzi, and A. Vitagliano, Gazz. Chim. Ital., 117 (1987) 445.
10 A. Gillie and J.K. Stille, J. Am. Chem. Soc., 102 (1980) 4933.
11 D. Milstein and J.K. Stille, J. Am. Chem. Soc., 101 (1979) 4981.
12 N. Chaudhury, M.G. Kekre, and R.J. Puddephatt, J. Organomet. Chem., 73 (1974) C17.

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Reactivity and Mechanism in Oxidative Addition to Palladium(II) and Reductive Elimination from Palladium(IV) and an Estimate of the Palladium–Methyl Bond Energy

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Oxidative addition of MeI to [$PdMe_2$(bpy)] (bpy = 2,2′-bipyridine) occurs by the S_N2 mechanism. Evidence includes the observation of second-order kinetics in acetone solvent, with a large negative value for the entropy of activation, and the observation of a cationic species, [$PdMe_3$(bpy)(CD_3CN)]$^+I^-$, in CD_3CN solvent. The reaction occurs more slowly than the analogous reaction of [$PtMe_2$(bpy)], but the same mechanism operates. Reductive elimination from [$PdIMe_3$(bpy)] to give ethane and [PdIMe(bpy)] follows good first-order kinetics, occurs more rapidly in polar solvents, and is strongly retarded by added iodide. These observations are interpreted in terms of a mechanism that involves preliminary ionization of iodide followed by reductive elimination from the cation [$PdMe_3$(bpy)]$^+$. Studies by differential scanning calorimetry allow an estimate of the Pd–C bond energy of ~130 kJ mol^{-1} to be obtained, and this value is considerably higher than the activation energy for reductive elimination of ethane from [$PdIMe_3$(bpy)]. The reductive elimination step is therefore concerted, and possible mechanisms, which may involve direct C–C coupling or C–C coupling after an agostic CHPd interaction, are discussed. This work is relevant to catalytic C–C coupling reactions using palladium complex catalysts.

Introduction

The catalysis by palladium complexes of the coupling reaction of organometals RM and organohalides R′X to give RR′ and MX is thought to be possible by oxidative addition–reductive elimination cycles involving either Pd(0)–Pd(II) or Pd(II)–Pd(IV) complexes.[2] Models for the former catalytic cycle have been developed,[3] but this has not been possible with Pd(II)–Pd(IV) systems since the proposed organopalladium(IV) intermediates could not be detected by spectroscopic methods.[4-7] The recent discovery of oxidative addition of methyl iodide to [$PdMe_2$(bpy)] (1) to give [$PdIMe_3$(bpy)] (2) which only slowly undergoes reductive elimination of ethane to give [PdIMe(bpy)] (3) (bpy = 2,2′-bipyridine) allows a study of the mechanisms of the reactions.[8-10]

Results

The Oxidative Addition Reaction. The reaction of [$PdMe_2$(bpy)] with MeI in CD_3CN was monitored by ^1H NMR. The reagents were mixed at −40 °C, and at this temperature resonances due to two products in ~3:1 ratio were observed. Resonances due to the major product [$PdIMe_3$(bpy)] were at δ 1.79 (PdMe trans to N) and 1.20 (PdMe trans to I); the second product was assigned to the ionic [$PdMe_3(CD_3CN)$(bpy)]$^+I^-$ with δ 1.61 (PdMe trans to bpy) and 1.06 (PdMe trans to CD_3CN), related to isolated cations involving tripodal nitrogen donor ligands such as [$PdMe_3$[tris(pyridin-2-yl)methane]]I.[9] Methyl group resonances for the cation broaden on warming, with coalescence at ≥−5 °C, but bpy resonances for the cation and all resonances for [$PdIMe_3$(bpy)] remain sharp, consistent with intramolecular exchange (scrambling) of methyl environments in the cation; on recooling to low temperature the original spectrum is obtained, with identical integration. At higher temperatures (≥15 °C) bpy resonances for the neutral and cationic complexes are coalesced, and the bpy and methyl resonances are broad compared to the sharp, growing resonances for the product [PdIMe(bpy)], indicating exchange between [$PdMe_3$(bpy)(CD_3CN)]$^+I^-$

(1) (a) University of Tasmania. (b) University of Western Ontario. (c) 3M Canada.
(2) For a recent review, see: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.
(3) Ozawa, F.; Fujimori, M.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1986**, *5*, 2144 and references therein.
(4) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4981.
(5) Loar, M. K.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4174.
(6) Moravsky, A.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4182.
(7) Kurosawa, H.; Emoto, M.; Urabe, A. *J. Chem. Soc., Chem. Commun.* **1984**, 968.
(8) Byers, P. K.; Canty, A. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1986**, 1722.
(9) Byers, P. K.; Canty, A. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1987**, 1093.
(10) Byers, P. K.; Canty, A. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1987**, *336*, C55.

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Table I. Second-Order Rate Constants for Oxidative Addition of MeI to [MMe_2(bpy)] in Acetone

M	T, °C	k_2, L mol^{-1} s^{-1}	E_a, kJ mol^{-1}	$\Delta S^{\ddagger}$ (20 °C), J K^{-1} mol^{-1}
Pd	3.0	1.75 ± 0.05		
Pd	10.3	2.25 ± 0.06		
Pd	20.0	3.23 ± 0.08		
Pd	30.0	4.65 ± 0.10	25.3 ± 0.6	−148 ± 2
Pt	−7.5	14 ± 1		
Pt	3.6	22 ± 1		
Pt	20	40 ± 1	24.9 ± 0.1	−129 ± 1

and [$PdIMe_3$(bpy)]. Because of this apparent equilibrium between the cationic and neutral palladium(IV) products (the same mixture is obtained by dissolution of [$PdIMe_3$(bpy)] in CD_3CN), the data do not prove that the cation is an intermediate in the formation of [$PdIMe_3$(bpy)]. Similar results have been obtained for oxidative addition of MeI to [$PtMe_2$(bpy)], but in this case the cation [$PtMe_3$(bpy)(CD_3CN)]$^+$ was formed and then decayed to [$PtIMe_3$(bpy)], thus providing good evidence for the S_N2 mechanism of oxidative addition.[11] Exchange between the cationic and neutral platinum(IV) compounds was slow on the NMR time scale at temperatures up to 0 °C, above which temperature the cationic intermediate was no longer detectable.[11]

In a similar reaction, CD_3I was added to [$PdMe_2$(bpy)] in acetone-d_6 solution at −60 °C. At this temperature signals due to [$PdMe_2$(bpy)] and [$PdIMe_2(CD_3)$(bpy)] were observed, but no ionic intermediate was detected. Resonances due to [$PdIMe_2(CD_3)$(bpy)] were observed for both Me trans to bpy and Me trans to I in a 2:1 intensity ratio. Hence scrambling of Me and CD_3 had already occurred. It is probable that the presumed ionic intermediate [$PdMe_2(CD_3)$(bpy)]$^+I^-$ undergoes Me for CD_3 scrambling before rearrangement to the product. The analogous reaction with [$PtMe_2$(bpy)] gives trans oxidative addition only, and a slow intramolecular Me, CD_3 scrambling reaction occurs subsequently.[11]

The kinetics of the oxidative addition in acetone solution, using at least an 8-fold excess of MeI, were monitored by UV–visible spectrophotometry. The oxidative addition was sufficiently fast that the subsequent reductive elimination of ethane did not interfere significantly. Good first-order kinetics were followed, and the observed first-order rate constants were directly proportional to the concentration of methyl iodide. Hence overall second-order kinetics were followed, first order in each reagent. For comparison, the oxidative addition to [$PtMe_2$(bpy)] was also studied and the activation parameters for both reactions were determined (Table I). The second-order rate constants for reaction with [$PdMe_2$(bpy)] and [$PtMe_2$(bpy)] at 20 °C were 3.23 ± 0.08 and 40.0 ± 0.1 L mol^{-1} s^{-1}, respectively, and the corresponding activation parameters were E_a = 25.3 ± 0.6 and 24.94 ± 0.06 kJ mol^{-1}, respectively, and $\Delta S^{\ddagger}$(20 °C) = −148 ± 2 and −129.0 ± 1.0 J K^{-1} mol^{-1}, respectively. The platinum complex reacts over 10 times as fast as the palladium analogue largely due to a less unfavorable $\Delta S^{\ddagger}$ term. All of the kinetic data, especially the large negative $\Delta S^{\ddagger}$ values, strongly support the S_N2 mechanism of oxidative addition in both cases.[2,11-14] The reactivity correlates with the energy of a metal (d_π) to bipyridine (π^*) charge-transfer transition in the UV–visible spectrum which lies at ~390 nm when M = Pd (a shoulder on the stronger π–π^* band of coordinated bpy) and at 470 nm when M = Pt. The higher energy d orbitals on [$PtMe_2$(bpy)] (see Figure 1) are more nucleophilic, and the complex reacts faster. A similar correlation within the platinum series [PtR_2(bpy)], with varying alkyl or aryl group R, has been noted previously.[14]

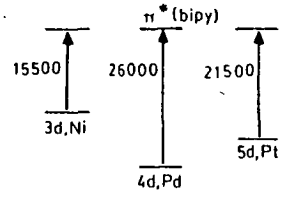


Figure 1. A qualitative MO energy level diagram for [MMe_2(bpy)]. The diagram assumes that the π^* levels of the 2,2′-bipyridine ligand are at the same energy when M = Ni, Pd, or Pt and hence places the levels for the Ni 3d, Pd 4d, or Pt 5d orbitals based on the energy of the respective metal to ligand charge-transfer transitions. The energies of the first MLCT bands are given in inverse centimeters.

The Reductive Elimination Reaction. The reductive elimination of ethane from [$PdIMe_3$(bpy)] could also be monitored readily by UV–visible spectrophotometry, using the increase in absorbance at 380 nm due to the palladium(II) product [PdIMe(bpy)]. Most work was carried out in acetone, in which the reductive elimination followed first-order kinetics. However, the mechanism was found to be fairly complex as described below. The observed rate constant at 20 °C was (6.24 ± 0.03) × 10^{-3} s^{-1}, and this was decreased only slightly to (3.65 ± 0.03) × 10^{-3} s^{-1} and (3.90 ± 0.02) × 10^{-3} s^{-1} in the presence of excess MeI and bpy, respectively. However, in the presence of excess NaI, the rate was greatly decreased to a limiting value of (1.45 ± 0.01) × 10^{-4} s^{-1}. This result strongly indicated that reductive elimination occurred to a major extent from the solvated cation [$PdMe_3$(bpy)]$^+$, and so a detailed study of the rate of reductive elimination as a function of iodide concentration was made. The results were consistent with the kinetic scheme shown in eq 1–4 This scheme leads

$$[PdIMe_3(bpy)] \xrightarrow{k_1} [PdIMe(bpy)] + C_2H_6 \quad (1)$$

$$[PdIMe_3(bpy)] \underset{k_3}{\overset{k_2}{\rightleftharpoons}} [PdMe_3(bpy)]^+ + I^- \quad (2)$$

$$[PdMe_3(bpy)]^+ \xrightarrow{k_4} [PdMe(bpy)]^+ + C_2H_6 \quad (3)$$

$$[PdMe(bpy)]^+ + I^- \xrightarrow{\text{fast}} [PdIMe(bpy)] \quad (4)$$

to the kinetic expression

$$-\frac{d}{dt}[2] = k_1[2] + k_2k_4[2]/(k_3[I^-] + k_4)$$

and gives the observed first-order rate constant $k_{obsd} = k_1 + k_2k_4/(k_3[I^-] + k_4)$ or $1/(k_{obsd} - k_1) = k_3[I^-]/k_2k_4 + 1/k_2$. An iterative treatment, Figure 2, was then used to give the values of k_1 = (1.45 ± 0.01) × 10^{-4} s^{-1}, k_2 = (6.1 ± 0.2) × 10^{-3} s^{-1}, and k_3/k_4 = (5.1 ± 0.3) × 10^4 L mol^{-1}. Hence, under the conditions of the kinetic experiments and in the absence of added iodide, 2.3% of the reductive elimination reaction occurs from [$PdIMe_3$(bpy)] and 97.7% from the cation [$PdMe_3$(bpy)]$^+$ or [$PdMe_3$(bpy)(acetone)]$^+$. Stable cations related to the intermediate [PdMe(bpy)]$^+$ or [PdMe(bpy)(acetone)]$^+$ have been reported recently,[10] in particular [PdMe(bpy)(MeCN)]$^+$[BF_4]$^-$.

If this mechanism is correct, the rate would be expected to depend on the solvent polarity, since the ionic intermediate should be formed more readily in polar solvents.

(11) Crespo, M.; Puddephatt, R. J. *Organometallics* **1987**, *6*, 2548. Scott, J. D.; Puddephatt, R. J. *Organometallics* **1985**, *4*, 1221.
(12) Monaghan, P. K.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.*, in press.
(13) Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1966**, *88*, 3511.
(14) Jawad, J. K.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1466.

Table II. First-Order Rate Constants for Reductive Elimination from [PdIMe$_3$(bpy)]

T, °C	[I$^-$], M	solvent	k_1, s^{-1}	E_a, kJ mol^{-1}	$\Delta S^\ddagger$ (20 °C), J K^{-1} mol^{-1}
4.0	0	acetone	$(8.4 \pm 0.1) \times 10^{-4}$		
10.0	0	acetone	$(1.35 \pm 0.1) \times 10^{-3}$		
20.0	0	acetone	$(6.25 \pm 0.03) \times 10^{-3}$		
30.2	0	acetone	$(7.8 \pm 0.1) \times 10^{-3}$	65 ± 13	−66 ± 34
20.0	3.6×10^{-2}	acetone	$(1.45 \pm 0.01) \times 10^{-4}$		
30.0	3.6×10^{-2}	acetone	$(5.27 \pm 0.03) \times 10^{-4}$		
40.0	3.6×10^{-2}	acetone	$(1.13 \pm 0.02) \times 10^{-3}$	78 ± 11	−53 ± 25
20.0	0	benzene	$(4.60 \pm 0.04) \times 10^{-4}$		
30.0	0	benzene	$(8.82 \pm 0.06) \times 10^{-4}$		
20.0	0	methanol	$(5.38 \pm 0.02) \times 10^{-3}$		
30.0	0	methanol	$(1.33 \pm 0.02) \times 10^{-2}$		
20.0	3.6×10^{-2}	methanol	$(1.95 \pm 0.02) \times 10^{-3}$		
30.0	3.6×10^{-2}	methanol	$(3.68 \pm 0.02) \times 10^{-3}$		
40.0	3.6×10^{-2}	methanol	$(5.47 \pm 0.06) \times 10^{-3}$	39 ± 5	−164 ± 17

Table III. First-Order Rate Constants for Reductive Elimination of [PdIMe$_3$(bpy) in Acetone Solution at 20 °C in the Presence of Iodide

10^3[NaI], M	$10^4 k_1$, s^{-1}	10^3[NaI], M	$10^4 k_1$, s^{-1}
0	62.5	1.008	2.27
0.103	5.66	1.20	2.09
0.206	3.74	2.015	2.11
0.412	3.10	2.67	1.89
0.667	2.54	4.03	1.72

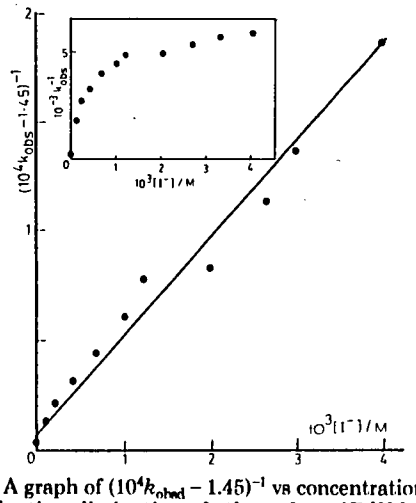


Figure 2. A graph of $(10^4 k_{obsd} - 1.45)^{-1}$ vs concentration of iodide for the reductive elimination of ethane from [PdIMe$_3$(bpy)] in acetone at 20 °C, where k_{obsd}/s^{-1} is the observed first-order rate constant for the reaction. The inset shows the corresponding plot of $(10^3 k_{obsd})^{-1}$ vs [I$^-$] which is clearly nonlinear but rises to a plateau value at high [I$^-$].

Observed first-order rate constants in the absence of added iodide at 30 °C were found to be $(0.882 \pm 0.002) \times 10^{-3}$ s^{-1}, $(7.8 \pm 0.1) \times 10^{-3}$ s^{-1}, and $(13.4 \pm 0.5) \times 10^{-3}$ s^{-1} in benzene, acetone, and methanol, respectively. These data are fully consistent with the proposed mechanism, the rates being faster in the more polar solvents.

Interestingly, the limiting rate of reaction in methanol at 20 °C in the presence of a large excess of iodide was $(1.95 \pm 0.01) \times 10^{-3}$ s^{-1} compared to the value $(1.45 \pm 0.01) \times 10^{-4}$ s^{-1} in acetone. This 13-fold increase in rate in methanol over acetone for the reaction of eq 1 was surprising and suggested that a polar intermediate or transition state might be involved. A study of the activation parameters for the reductive elimination reaction was therefore undertaken. In the absence of added iodide the observed parameters with acetone solvent were $E_a = 65 \pm 13$ kJ mol^{-1} and $\Delta S^\ddagger$ (20 °C) = -66 ± 34 J K^{-1} mol^{-1}. The large standard deviations arise because of the sensitivity of the observed rate constant to trace impurities that retard the reaction and hence the difficulties in obtaining good reproductibility under these conditions. The negative value of $\Delta S^\ddagger$ is consistent with formation of a polar intermediate (eq 2) since much greater solvent ordering would occur for the ionic intermediate. Activation parameters were also determined for the reactions in the presence of a large excess of iodide, so that the parameters are those for the reaction of eq 1. Values in acetone and methanol, respectively, were $E_a = 78 \pm 11$ and 39 ± 5 kJ mol^{-1} and $\Delta S^\ddagger = -53 \pm 25$ and -164 ± 17 J K^{-1} mol^{-1}. Again these values strongly suggest a polar intermediate or transition state and are not consistent with a nonpolar concerted reductive elimination. A likely explanation of these data is that at least partial ionization of iodide occurs before reductive elimination of ethane. Thus, the precursor state to reductive elimination could be a polar species [Me$_3$(bpy)Pd$^{\delta+}$···I$^{\delta-}$], or it could be a tight ion pair [Me$_3$(bpy)Pd]$^+$I$^-$. In neither case would inhibition by iodide occur, but both species are highly polar and would cause the solvent ordering required by the negative $\Delta S^\ddagger$ values.

Thus although the kinetic studies indicate a two-term rate law, one retarded by free iodide and the other not, it is probable that ionization of the PdI bond is important in both cases and that reductive elimination from the cationic or partially cationic intermediate occurs relatively easily.

The complex [PtIMe$_3$(bpy)] is very stable and decomposes only at ~270 °C to give methane as the major product. Hence it is not possible to compare the mechanisms in this case. The complexes [PtIMe$_3$L$_2$] (L = tertiary phosphine) undergo reductive elimination by a mechanism involving reversible phosphine dissociation followed by loss of ethane from the neutral five-coordinate species [PtIMe$_3$L].[15] Thus it seems general that reductive elimination from d^6 complexes is easier from intermediates with coordination number five. A rationalization of this observation has been given.[15]

The general observations above have been confirmed by monitoring the kinetics of the reductive elimination by ^{1}H NMR spectroscopy. These experiments were carried out by using 0.02 M solutions of [PdIMe$_3$(bpy)] in acetone-d_6, prepared in situ by reaction of [PdMe$_2$(bpy)] with excess MeI, at temperatures from 9 to 25 °C. Good first-order kinetics were followed, the rates were greater in the presence of water to increase the solvent polarity, and the rates were retarded in the presence of free iodide.

The Palladium–Carbon Bond Energy. The reductive elimination of ethane from [PdIMe$_3$(bpy)] to give [PdIMe(bpy)] occurs very cleanly in the solid state,[8] and the reaction has now been monitored by differential scanning calorimetry (DSC). A typical DSC scan is given

(15) Brown, M. P.; Puddephatt, R. J.; Upton, C. E. E. *J. Chem. Soc., Dalton Trans.* **1974**, 2457.

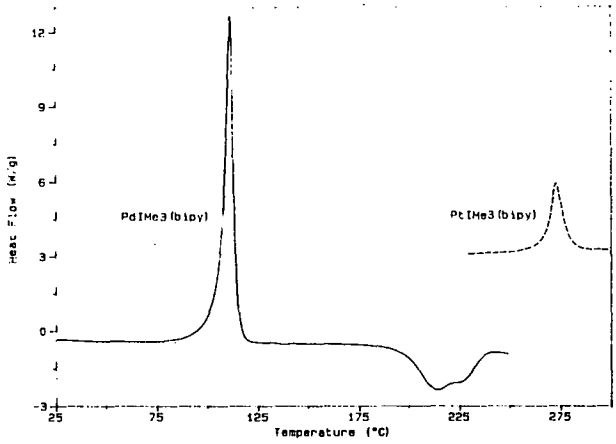


Figure 3. Differential scanning calorimetry for the decomposition of (a) $[PdIMe_3(bpy)]$ and (b) $[PtIMe_3(bpy)]$.

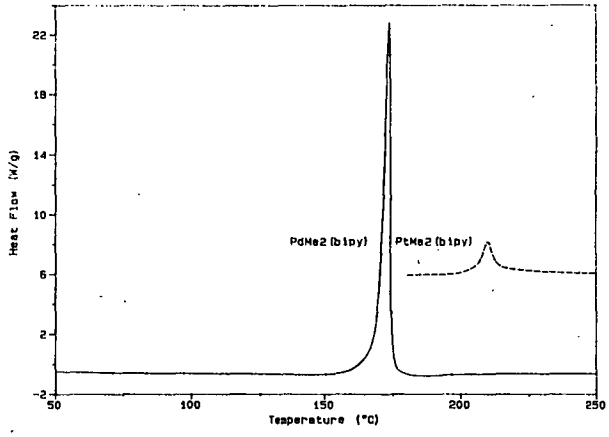


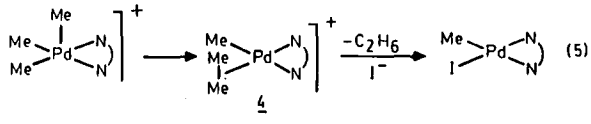
Figure 4. Differential scanning calorimetry for the decomposition of (a) $[PdMe_2(bpy)]$ and (b) $[PtMe_2(bpy)]$.

in Figure 3. Decomposition began at ~80 °C and was complete at ~120 °C, giving a very clean exotherm. Weight loss was calculated to be 6.9% and found to be 7.3 ± 0.2%, and the product was confirmed to be pure [PdIMe(bpy)] by NMR. Further general decomposition occurred at 180–240 °C (Figure 3). The integrated area of the exotherm centered at ~110 °C gave $\Delta H = -105 \pm 2$ kJ mol^{-1}. An approximation to the mean Pd–Me bond energy can then be obtained if it is assumed that this enthalpy change corresponds only to formation of the C–C bond of ethane (368 kJ mol^{-1}) and loss of two Pd–Me bonds. The nature of the approximations has been discussed elsewhere.[16] Hence D(PdMe) = $^1/_2(368 - 105)$ = 131.5 ± 6 kJ mol^{-1}. This appears to be the first estimate of a Pd–C bond energy. The Pd–C bonds are reasonably strong and may be compared with a value of D(PtMe) in $[PtIMe_3(PMe_2Ph)_2]$ of 144 kJ mol^{-1} determined by DSC.[15] The Pt–Me bond is slightly stronger.[17]

For comparison, a DSC study of the thermolysis of $[PtIMe_3(bpy)]$ was carried out (Figure 3). Decomposition occurred giving an exotherm over the region 240–300 °C, with a peak at 273 ± 2 °C. However, the weight loss was 11%, compared to the theoretical value of 5.7% for loss of ethane, and the major product was methane. Clearly, this is not a simple reductive elimination reaction, and so the Pt–Me bond energy could not be determined. The difference in thermal stabilities of the precursors $[MMe_2(bpy)]$ (M = Pd or Pt) is much less as shown in Figure 4, though decomposition of the palladium complex is more exothermic.

Conclusions

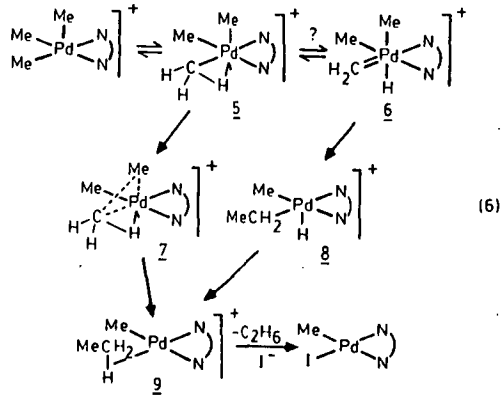
Both the oxidative addition and reductive elimination studied in this work appear to involve the intermediacy of the solvated cation $[PdMe_3(bpy)]^+$, at least to a major extent in solution reactions. The reductive elimination of ethane is intramolecular, and we note that the apparent activation energy E_a for reductive elimination in acetone or methanol is much lower (E_a values 65 kJ mol^{-1} in acetone, 78 kJ mol^{-1} in acetone with excess I$^-$, 39 kJ mol^{-1} in methanol with excess I$^-$) than the estimated Pd–Me bond energy of ~130 kJ mol^{-1}. Although iodide dissociation is implicated in the reductive elimination, this step is unlikely to affect the Pd–Me bond energy significantly.[18] Hence the actual reductive elimination must be a concerted process and could occur in a similar way to that proposed earlier for reductive elimination from platinum(IV) (eq 5).[15]



(5)

4

However, in view of the more recent evidence that α-elimination can occur readily and reversibly from coordinatively unsaturated metal alkyl derivatives[19] and that C–C bond activation in both homogeneous and heterogeneous conditions may necessarily occur after C–H activation,[19,20] an alternative mechanism should also be considered (eq 6).



(6)

5 6 7 8 9

Migration of a methyl to a methylene group is well-established,[2] and the mechanism accounts in a rational way for the need for a vacant coordination site prior to reductive elimination. Either mechanism of eq 5 or eq 6

(16) It is important to note that, although the thermochemical data for the solid state are precise, the correction to the gas phase depends on assumptions that cannot be verified. Hence the error limits to E(PdC) are minimum values. Mortimer, C. T.; McNaughton, J. L.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1972**, 1265 and references therein.

(17) In the isostructural Pd(IV) and Pt(IV) complexes $[MMe_3\{tris(pyrazol-1-yl)methane\}]I$, the Pd–C and Pt–C bond lengths are similar,[9] and in the complexes *cis*-$[MMe_2(PMePh_2)_2]$, the M–C bond is slightly shorter and the M–P bond slightly longer when M = Pd compared to when M = Pt. Again this supports a strong Pd–C bond. Wisner, J. M.; Bartczak, T. J.; Ibers, J. A. *Organometallics* **1985**, *5*, 2044.

(18) Although other factors are present, it is of interest to note here that the iodide salt of the closely related cation $[PdMe_3\{tris(pyridin-2-yl)methane\}]^+$ is more stable than $[PdIMe_3(bpy)]$ both in the solid state and in chloroform solution.[9]

(19) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

(20) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 7272. For activation of ethane at a Pt surface, see: Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980; p 181.

appears to be consistent with the experimental data reported here. We note that, in eq 6, α-elimination to give 6 need not occur prior to C–C bond formation since the agostic interaction[19] in 5 involves a rocking motion which will facilitate (and could be concurrent with) C–C bond formation, as shown in 7.[21] Steric hindrance to C–C bond formation should therefore be less than in complex 4 of eq 5. Intermediate 7 is favored over 8 since the latter could reductively eliminate methane or ethane or β-eliminate ethylene and so would not be expected to give the high observed selectivity for formation of ethane.[21]

The rates of reaction and the activation parameters for oxidative addition of MeI to [$PdMe_2$(bpy)] and [$PtMe_2$(bpy)] are similar, with the platinum complex being the more reactive. The mechanisms are clearly the same, namely, the S_N2 mechanism, for both systems. However, reductive elimination of ethane occurs easily for [$PdIMe_3$(bpy)] but does not occur at all for [$PtIMe_3$(bpy)]. This major difference in reactivity is not due to a large difference in M–Me bond energies in the two complexes but is due to a much lower activation energy for concerted reductive elimination for the palladium complex.[22] The platinum(IV) complex forms stable complexes [$PtMe_3$(bpy)S]$^+$ (S = acetone or MeCN) which do not reductively eliminate ethane whereas the analogous palladium cations do so very readily.

We note that the above oxidative addition–reductive elimination reactions provide a good model for catalytic C–C coupling reactions via the Pd(II)–Pd(IV) cycle.[4-7] However, since the diimine ligands used here favor Pd(IV) whereas the phosphine ligands used in the catalytic reactions favor Pd(0), caution should be exercised in extrapolation to the catalytic reactions. Nevertheless, if the Pd(II)–Pd(IV) cycle is correct, the detailed mechanisms of the oxidative addition and reductive elimination steps may be similar to those established in this work.

Experimental Section

^{1}H NMR spectra were recorded by using a Bruker AM-300 spectrometer, and kinetic studies were carried out by using a Varian CARY 2290 spectrometer, with temperature control using a Polyscience Series 900 constant temperature bath. Differential scanning calorimetry was carried out by using a Du Pont Instruments 912 DSC in conjunction with the 9900 computer/thermal analyzer. All samples were run in uncrimped, closed Al pans under N_2 atmosphere, purging at 20 mL min^{-1}. The scan rate was 20 °C min^{-1}, and calibration was with In metal. The error limits given are standard deviations from six independent runs.

[$PdMe_2$(bpy)] and [$PdIMe_3$(bpy)] were prepared by the reported method.[8,10]

[$PdMe_2$(bpy)] with MeI in CD_3CN. An NMR tube containing [$PdMe_2$(bpy)] (10 mg) in CD_3CN (0.5 mL) was cooled to −45 °C, and MeI (6 μL) was added. The ^{1}H NMR spectrum at −40 °C contained resonances due to *fac*-[$PdIMe_3$(bpy)], δ 1.79 (s, 2 Me, Me trans to N) and 1.20 (s, 1 Me, Me trans to I), and additional peaks assigned to *fac*-[$PdMe_3(CD_3CN)$(bpy)]$^+$, δ 1.61 (s, 2 Me, Me trans to bpy) and 1.06 (s, 1 Me, Me trans to CD_3CN). Further details are given in the text.

[$PdMe_2$(bpy)] with CD_3I in Acetone-d_6. A solution of [$PdMe_2$(bpy)] (10 mg) in acetone-d_6 (0.5 mL) in an NMR tube was cooled to −60 °C, and CD_3I (6 μL) was added. At −60 °C, the ^{1}H NMR spectrum contained resonances due to [$PdMe_2$(bpy)] and [$PdIMe_2(CD_3)$(bpy)], but no ionic intermediate was detected. The resonances due to [$PdIMe_2(CD_3)$(bpy)] gave the ratio Me trans to N:Me trans to I = 2:1, showing that the oxidative addition was not stereospecific.

Kinetic Studies of Oxidative Addition by UV–Visible Spectrophotometry. A solution of [$PdMe_2$(bpy)] in acetone (3 mL, 3×10^{-4} M) in a cuvette was thermostated at 20.0 °C, and a known excess of MeI was added by using a microsyringe. After rapid stirring, absorbance values at λ = 440 nm were collected at 0.1-min intervals for 10 min, at which time reaction was complete. Computer treatment of the data showed good first-order kinetics from which the observed first-order rate constants and standard deviations were obtained. A plot of k_{obsd} vs [MeI] was linear, and the slope gave the second-order rate constant. The same method was used at other temperatures, and the activation parameters were obtained from the Arrhenius equation.

The oxidative addition to [$PtMe_2$(bpy)] was monitored in a similar way but with λ = 452 nm.

Kinetic Studies of Reductive Elimination by UV–Visible Spectrophotometry. A freshly prepared solution of [$PdIMe_3$(bpy)] (purified and stored in the dark at −20 °C) in acetone (3 mL, 3×10^{-4} M) was transferred to a cuvette and thermostated to 20.0 °C in the cell compartment of the spectrophotometer. Absorbance values at λ = 380 nm were collected at 0.2-min intervals for 1 h. Computer treatment showed good first-order kinetics from which the first-order rate constant and standard deviation were calculated. The same method was used to determine rate constants at higher temperatures, and activation parameters were determined from the Arrhenius equation.

The same method was used to collect data in benzene or methanol solvents and in the presence of additives.

Acknowledgment. We thank the ARGS (Australia) and NSERC (Canada) for financial support.

Registry No. 1, 95841-49-9; *fac*-2, 110182-93-9; *fac*-[$PdMe_3(CD_3CN)$(bpy)]$^+$, 113748-25-7; [$PdIMe_2(CD_3)$(bpy)], 113748-26-8; [$PtMe_2$(bpy)], 52594-52-2.

(21) The difficulty of direct C–C, compared to C–H or H–H, reductive elimination has been rationalized by theoretical studies. In particular, high level GVB calculations of the transition state for reductive elimination of ethane from $PdMe_2$ or $PtMe_2$ predict that the methyl groups should be tilted by 39° and 51°, respectively, leading to a geometry similar to that in the classic agostic $TiCH_3$ unit.[19] Thus, although the agostic $PdCH_3$ interaction was not explicitly discussed, it is implicitly predicted by the GVB calculations. Low, J. J.; Goddard, W. A. *Organometallics* **1986**, *5*, 609. Low, J. J.; Goddard, W. A. *J. Am. Chem. Soc.* **1986**, *108*, 6115.

(22) GVB calculations on $MCl_2Me_2(PH_3)_2$ predict similar intrinsic M–Me bond energies of 51 and 52 kcal mol^{-1} but significantly different average adiabatic bond energies of 31.7 and 10.0 kcal mol^{-1}, when M = Pt and Pd, respectively. The activation energies for reductive elimination were calculated to be 34.9 kcal mol^{-1} and zero for M = Pt and Pd, respectively.[21]

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Organopalladium(IV) Chemistry: Oxidative Addition of Organohalides to Dimethylpalladium(II) Complexes to form Ethyl, σ-Benzyl, and σ-Allylpalladium(IV) Complexes

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The first examples of ethyl, σ-benzyl, and σ-allylpalladium(IV) complexes are formed on oxidative addition of organohalides to $PdMe_2$\{(pyridin-2-yl)bis(*N*-methylimidazol-2-yl)methane\} [$PdMe_2$\{(py)$(mim)_2CH$\}]; the complexes [*fac*-$PdRMe_2$\{(py)$(mim)_2CH$-*N*,*N*′,*N*″\}]X (RX = EtI, $PhCH_2Br$, CH_2=$CHCH_2Br$) are stable at ambient temperature, with the cations present as two isomers, and benzyl bromide also forms the neutral complex *fac*-$Pd(CH_2Ph)Me_2$(bipy)Br on oxidative addition to $PdMe_2$(2,2′-bipyridyl), but EtI and CH_2=$CHCH_2Br$ form transient Pd^{IV} species, detectable by ^1H n.m.r. spectroscopy, prior to reductive elimination reactions.

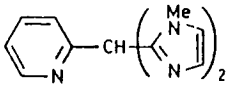
Although organoplatinum(IV) chemistry has developed steadily following the report of $[PtMe_3(\mu_3\text{-}I)]_4$ in 1907,[1] aryl- and alkyl-palladium(IV) compounds are limited to mono- and bis-pentafluorophenylpalladium(IV) complexes,[2] and recently reported trimethylpalladium(IV) complexes,[3—5] respectively. The $Pd^{IV}Me_3$ complexes, formed by oxidative addition of iodomethane to $Pd^{II}Me_2$ complexes, undergo reductive elimination in solution to form $Pd^{II}Me$ complexes and ethane, except for some cationic species involving tripodal nitrogen donor ligands, *e.g.* [*fac*-$PdMe_3$\{tris(pyridin-2-yl)methane\}].[4] In view of this we have attempted to expand organopalladium(IV) chemistry *via* synthesis of cationic complexes,

resulting in isolation of the first complexes containing ethyl, benzyl, and allyl groups, and thus demonstrating potential for development of an extensive organometallic chemistry of palladium(IV).

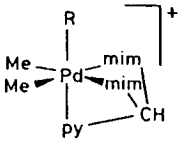
The stability of cations $[PdMe_3L_n]^+$ increases with increasing donor ability of the ligand,[4] and thus to maximize opportunities for isolation of $Pd^{IV}RMe_2$ complexes the new ligand (pyridin-2-yl)bis(*N*-methylimidazol-2-yl)methane [(py)(mim)$_2$CH] was synthesized,† since the tripods studied to date contain pyridin-2-yl groups only [(py)$_3$CH] or at least two weakly basic pyrazol-1-yl (pz) groups[4] with the order of donor ability of the groups mim > py > pz,[5] and the presence of two donor types is expected to facilitate interpretation of n.m.r. spectra of reaction products.

Experiments at ambient temperature, with reactions followed by ^{1}H n.m.r. spectroscopy, indicated immediate formation of [*fac*-$PdRMe_2$\{(py)(mim)$_2$CH\}]$^+$ on addition of excess of organohalide (RX = EtI, $PhCH_2Br$, CH_2=CH-CH_2Br) to $PdMe_2$\{(py)(mim)$_2$CH\} in $(CD_3)_2CO$, without subsequent reductive elimination, and the complexes were then prepared in high yield from the substrate $[PdMe_2(pyridazine)]_n$[5] in acetone by direct addition of [(py)(mim)$_2$CH] followed by RX and addition of hexane; a $Pd^{IV}Me_3$ complex was isolated (oxidative addition of MeI) for comparison of spectra.‡ The complexes are the most stable organopalladium(IV) complexes isolated to date, with no reductive elimination being detected on heating to *ca.* 60 °C in $(CD_3)_2CO$.

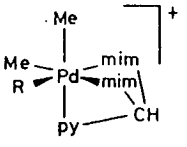
For the isolated cations [*fac*-$PdRMe_2$\{(py)(mim)$_2$CH\}]$^+$ in $CDCl_3$, two isomers, (**A**) and (**B**), are present in a similar ratio to that observed for the oxidative addition in $(CD_3)_2CO$ (as followed by n.m.r.): *ca.* 1 : 1 ratio for the benzyl complex, *ca.* 5 : 3 for the ethyl complex, and *ca.* 6 : 5 for the allyl complex.



(py)(mim)$_2$CH



(A)



(B)

Structures of (**A**) and (**B**) are readily assigned directly from spectra, in particular integration of ligand, Me, and R resonances, and the presence of inequivalent $PdCH_2$ protons for the ethyl, benzyl, and allyl complexes of isomer (**B**) owing to chirality at the palladium centre in (**B**), *e.g.* as shown in Figure 1 for the allyl complex.

In contrast to $PdMe_2$\{(py)(mim)$_2$CH\}, the bidentate ligand complex $PdMe_2$(2,2′-bipyridyl) on reaction with EtI and CH_2=$CHCH_2Br$ gave spectra showing the presence of only trace amounts (decreasing with time) of a Pd^{IV} intermediate with formation of reductive elimination products. The ethyl iodide intermediate formed ethane, propane, and PdR(bipy)I (R = Me, Et), and the allyl bromide intermediate formed ethane, PdMe(bipy)Br, and an insoluble solid of analytical composition $Pd(C_3H_5)$(bipy)Br.§ At −10 °C EtI did not react with $PdMe_2$(bipy), but CH_2=$CHCH_2Br$ gave a spectrum showing a high yield of $Pd(CH_2CH{=}CH_2)Me_2$(bipy)Br, *e.g.* δ 5.28 (m, CH, partly obscured by excess allyl bromide), 4.47 (dd, CH_{trans}, ^3J 16.88, ^2J 2.37 Hz), 4.37 (dd, CH_{cis}, ^3J 9.83, ^2J 2.38 Hz), 2.50 (dd, $PdCH_2$, ^3J 8.70, ^4J 0.98 Hz), 1.75 (s, $PdMe_2$) for the $Pd^{IV}(CH_2CH{=}CH_2)Me_2$ group, together with reductive elimination products, but the complex could not be isolated. However, benzyl bromide gave the isolable complex *fac*-$Pd(CH_2Ph)Me_2$(bipy)Br, the first organopalladium(IV) bromo-complex, which is more stable than the first reported neutral complex *fac*-$PdMe_3$(bipy)I,[3] undergoing reductive elimination over *ca.* 120 min at ambient temperature in $CDCl_3$ compared with *ca.* 30 min for the latter.

These results indicate that it is now possible to develop a wide-ranging organometallic chemistry of palladium(IV) to complement the well established chemistry of this oxidation state for platinum, and that tripodal nitrogen donor ligands, in particular [(py)(mim)$_2$CH], may have an important role in developing high oxidation state organometallic chemistry. Aspects of the reactivity of organopalladium(II) and organopalladium(IV) compounds reported here are relevant to the

† Synthesised by reduction of (mim)$_2$CO to (mim)$_2$CH$_2$ [as for (py)$_2$CO to (py)$_2$CH$_2$],[6] followed by reaction with PhLi and 2-bromopyridine [as for (py)$_2$CH$_2$ to (py)$_3$CH],[7] m.p. 137—138 °C, δ (Me_4Si, in $CDCl_3$): 8.56 [1H, ddd, H(6)$_{py}$, ^3J 4.90, ^4J 1.83, ^5J 0.93 Hz], 7.69 [1H, ddd, H(4)$_{py}$, $^3J_{4,5}$ ~$^3J_{3,4}$ ~7.66, ^4J 1.84 Hz], *ca.* 7.26 [H(3)$_{py}$, (obscured by $CHCl_3$)], 7.20 [1H, ddd, H(5)$_{py}$, $^3J_{5,6}$ 4.88, $^3J_{4,5}$ 7.34, ^4J 1.11 Hz], 7.00 [2H, d] and 6.87 [2H, d, H(4,5)$_{mim}$, $^3J_{4,5}$ 1.23 Hz], 5.95 [1H, s, CH], 3.47 [3H, s, NCH_3].

‡ The Pd^{IV} complexes (formed in 58—76% yield) and $PdMe_2$\{(py)(mim)$_2$CH\} {prepared from $[PdMe_2(pyridazine)]_n$[5] and the ligand in acetone, with addition of hexane, 76% yield} have satisfactory microanalyses (C, H, N) and ^{1}H n.m.r. spectra (300 MHz), and $Pd(CH_2Ph)Me_2$(bipy)Br has molecular weight 527 (osmometric in chloroform at 25 °C, calc. 510). ^{1}H N.m.r. spectra for the $Pd^{II}Me_2$ and $Pd^{IV}RMe_2$ groups in the isolated complexes are given, with relative intensities appropriate for the isomer ratios, and ligand resonances as expected, including two environments in the Pd^{IV} cations that form isomers.

$PdMe_2$\{(py)(mim)$_2$CH\}: δ [Me_4Si, in $(CD_3)_2CO$] 0.03 [6H, s, PdMe].

[$PdMe_3$\{(py)(mim)$_2$CH\}]I: δ [Me_4Si, in $CDCl_3$] 1.55 [3H, s, Me], 1.33 [6H, s, Me].

[$PdEtMe_2$\{(py)(mim)$_2$CH\}]I: 2.56 [2H, q, CH_2(A), ^3J 7.53 Hz], 2.32 [1H, m, CH*H*(B)] and 2.28 [1H, m, C*H*H(B), ^2J ~^3J 7.57 Hz], 1.55 [3H, s, PdMe(B)], 1.30 [6H, s, PdMe(A)], 1.29 [3H, s, PdMe(B)], 1.09 [3H, t, CH_3(A)], 1.02 [3H, t, CH_3(B)].

[$Pd(CH_2Ph)Me_2$\{(py)(mim)$_2$CH\}]Br: *ca.* 7.2—6.8 [5H, m, Ph(A,B)], 3.67 [2H, s, CH_2(A)], 3.57 [1H, d, CH*H*(B)] and 3.29 [1H, d, C*H*H(B), ^2J 8.36 Hz], 1.66 [3H, s, PdMe(B)], 1.46 [6H, s, PdMe(A)], 1.44 [3H, s, PdMe(B)].

[$Pd(CH_2CH{=}CH_2)Me_2$\{(py)(mim)$_2$CH\}]Br: 5.84 [1H, m, CH=(A,B)], 5.07 [1H, m, CH*H cis* to CH=(A,B)], 5.25 [1H, m, CH*H trans* to CH=(A,B)], 3.16 [2H, d, $PdCH_2$(A), ^3J 8.16 Hz], 2.93 [2H, m, $PdCH_2$(B)], 1.62 [3H, s, PdMe(B)], 1.40 [6H, s, PdMe(A)], 1.38 [3H, s, PdMe(B)].

$Pd(CH_2Ph)Me_2$(bipy)Br: 6.73 [1H, t, H(4)], 6.60 [2H, t, H(3,5)], 6.40 [2H, d, H(2,6)], 3.17 [2H, s, $PdCH_2$], 1.98 [6H, s, PdMe].

§ The complexes PdMe(bipy)X (X = Br,[5] I[3,9]) have been synthesized independently from $Pd^{II}Me$ substrates, and their spectra reported. The complex $Pd(C_3H_5)$(bipy)Br is too insoluble for n.m.r. characterization, and probably has the structure $[(\eta^3\text{-}C_3H_5)Pd(bipy)]^+Br^-$, in view of the proposal that the insoluble chloro analogue has this structure,[10] and spectroscopic and structural studies of related complexes, *e.g.* the η^3-2-methylpropenyl complex $[(\eta^3\text{-}C_4H_7)Pd(pyridine)_2]^+BF_4^-$,[11] and the tetramethylethylenediamine complex $[(\eta^3\text{-}C_3H_5)Pd(tmeda)]^+[(\eta^3\text{-}C_3H_5)PdCl_2]^-$.[12] The other expected reductive elimination product from the allyl bromide reaction, but-1-ene, was not detected, owing to the complexity of the n.m.r. spectrum in the high field region and the expected low yield of but-1-ene [*ca.* 20% of reductive elimination product, estimated from ethane : PdMe(bipy)Br relative integration].

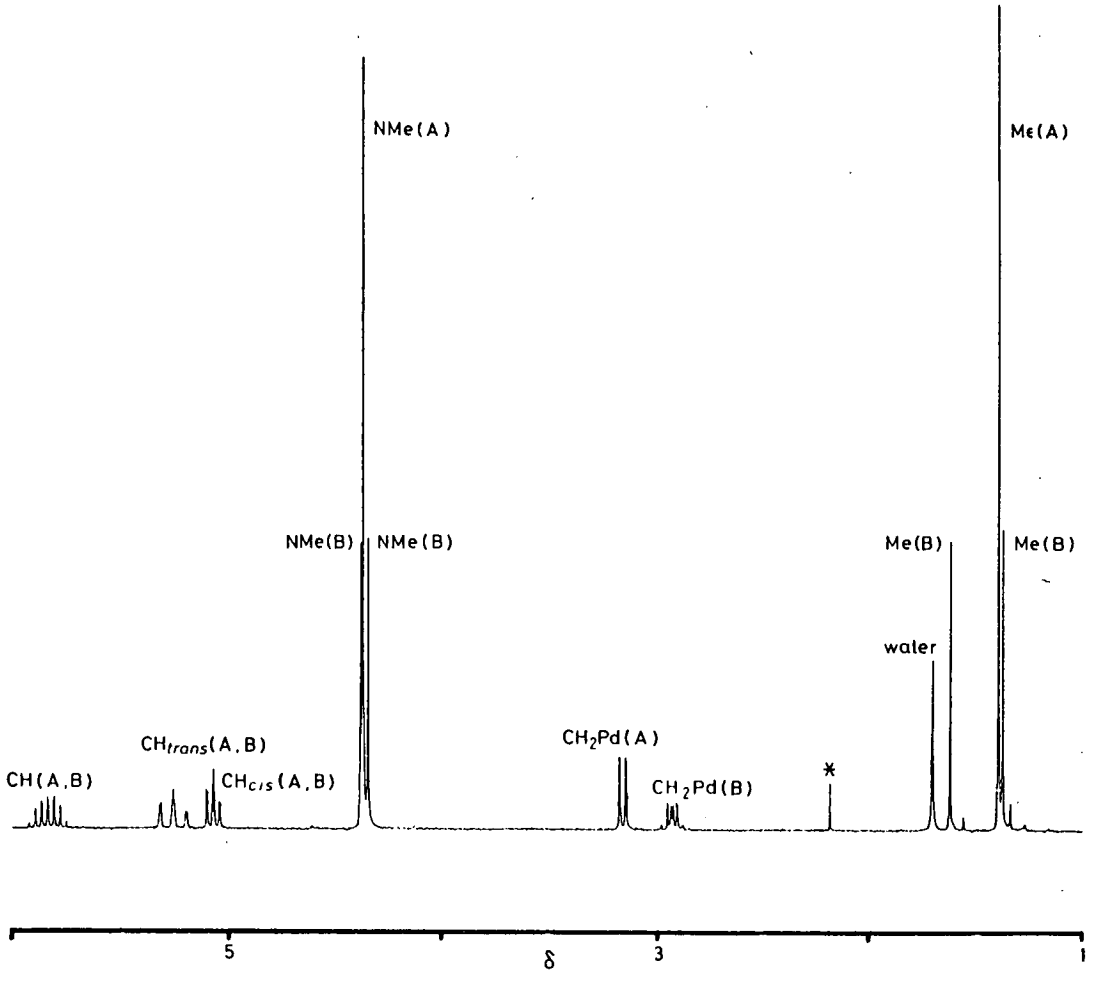


Figure 1. ^{1}H n.m.r. spectrum of [*fac*-Pd(CH$_2$CH=CH$_2$)Me$_2$\{(py)(mim)$_2$CH\}]Br in $CDCl_3$, in the region showing the Pd^{IV}-(CH$_2$CH=CH$_{cis}$CH$_{trans}$)Me$_2$ groups and methyl groups of the *N*-methylimidazol-2-yl rings, with assignment as isomer (**A**) or (**B**) indicated; H$_{cis}$ and H$_{trans}$ refer to the orientation with respect to the =CH proton; * is an impurity in the solvent.

possible role of Pd^{IV} in organic synthesis and catalysis,[13,14] in particular the feasibility of neutral intermediates 'PdR'R$_2$-L$_2$X' in some coupling reaction systems to form R'R and R$_2$.[14]

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References

1 W. J. Pope and S. J. Peachey, *Proc. Chem. Soc.*, 1907, **23**, 86; *J. Chem. Soc.*, 1909, 571.
2 R. Uson, J. Fornies, and R. Navarro, *Synth. React. Inorg. Metal-Org. Chem.*, 1977, **7**, 235; *J. Organomet. Chem.*, 1975, **96**, 307.
3 P. K. Byers, A. J. Canty, B. W. Skelton, and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1986, 1722.
4 P. K. Byers, A. J. Canty, B. W. Skelton, and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1987, 1093.
5 P. K. Byers, A. J. Canty, B. W. Skelton, and A. H. White, *J. Organomet. Chem.*, 1987, **336**, C55.
6 G. R. Newkome, V. K. Gupta, H. C. R. Taylor, and F. R. Fronczek, *Organometallics*, 1984, **3**, 1549.
7 A. J. Canty, N. Chaichit, B. M. Gatehouse, E. E. George, and G. Hayhurst, *Inorg. Chem.*, 1981, **20**, 2414.
8 A. J. Canty and C. V. Lee, *Organometallics*, 1982, **1**, 1063.
9 P. K. Byers and A. J. Canty, *Inorg. Chim. Acta*, 1985, **104**, L13.
10 G. Paiaro and A. Musco, *Tetrahedron Lett.*, 1965, 1583.
11 B. Akermark, B. Krakenberger, S. Hansson, and A. Vitagliano, *Organometallics*, 1987, **6**, 620.
12 L. S. Hegedus, B. Akermark, D. J. Olsen, O. P. Anderson, and K. Zetterberg, *J. Am. Chem. Soc.*, 1982, **104**, 697.
13 For a recent report proposing undetected organopalladium(IV) intermediates, see, for example, a report of the coupling of acetylenes to form enynes: B. M. Trost, C. Chan, and G. Ruhter, *J. Am. Chem. Soc.*, 1987, **109**, 3486.
14 D. Milstein and J. K. Stille, *J. Am. Chem. Soc.*, 1979, **101**, 4992; A. Gillie and J. K. Stille, *ibid.*, 1980, **102**, 4933; M. K. Loar and J. K. Stille, *ibid.*, 1981, **103**, 4174; A. Moravskiy and J. K. Stille, *ibid.*, 1981, **103**, 4182.